Part B, Volume 1, No. 9, September 1963

Journal of Polymer Science, Part B

Polymer Letters

Editorial Board: R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

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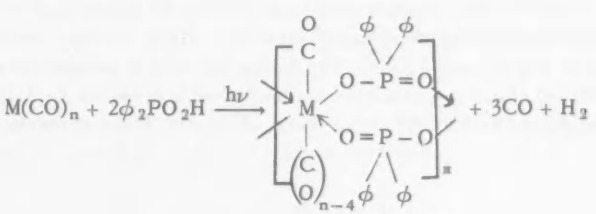
POLYMER LETTERS VOL. 1, PP. 457-459 (1963)

A NOVEL SYNTHESIS OF TRANSITION METAL COORDINATION POLYMERS

We have recently reported a novel reaction of metal carbonyls involving their photochemical oxidative decarbonylation by an organic active hydrogen compound, such as a β-diketone or 8-hydroxyquinoline, to produce the corresponding metal chelate (1).

$$M(CO)_n + 3\ LH \xrightarrow{h\nu} ML_3 + nCO + 3/2\ H_2$$

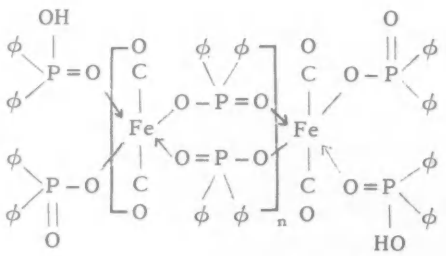
We now wish to report an important extension of this reaction to certain inorganic active hydrogen compounds such as diphenylphosphinic acid, in particular, to produce interesting metal diphenylphosphinate coordination polymers.



The specific polymers prepared by this novel and convenient method resemble in part those of Block, Simkin, and Ocone (2) prepared by melt polymerization of the metal acetylacetonate and diphenylphosphinic acid. The specific features of our route are (1) mildness of conditions, i.e., moderate temperatures, facilitated by the use of ultraviolet radiation, such that crosslinking possibilities are minimized, (2) evolution of CO and H_2 accompanied by oxidation of the metal to a stable oxidation state to act as driving forces for extensive reaction, (3) presence of residual CO ligands or other selected ligands in the linear polymer to provide a means for subsequent controlled crosslinking, and (4) broad scope with respect to the synthesis of different polymer structures.

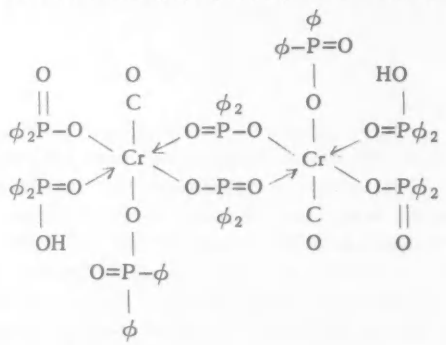
Reaction of $Fe(CO)_5$ with diphenylphosphinic acid at a 1:2 molar ratio in refluxing tetrahydrofuran under ultraviolet irradiation from a 250 watt GE sunlamp yielded an intractable (insoluble) white solid which was stable up to 300°C. and was insoluble in water. Treatment with concentrated HCl yielded $2\phi_2PO_2H/Fe$, and with Br_2/pyridine it yielded 1.5–20 CO/Fe. Its infrared spectrum (KBr disk) showed the presence of Fe–CO and ϕ–P with slight or no free P–OH or free P=O. The elemental and infrared analysis and degradative studies suggest the presence

of the following repeating unit in the solid product.

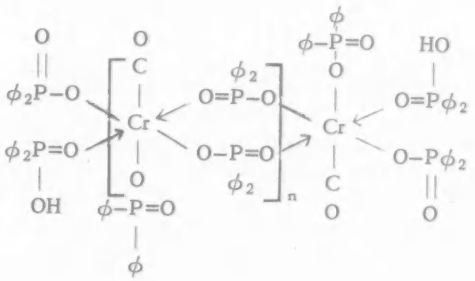


It may be noted that the total number of electrons about iron in this structure is that of the next inert gas, Kr.

Reaction of $Cr(CO)_6$ with diphenylphosphinic acid in refluxing toluene under similar conditions provided a number of chloroform and benzene soluble fractions, all of which were stable at least up to 300°C. and insoluble in water. The products obtained by soxhlet extraction with ethanol, benzene, and chloroform varied from crystalline through coherent film-like to waxy green solids. The lowest molecular weight (osmometric in $CHCl_3$) crystalline fraction approximated a dimer of the following structure, based on elemental (C, H, Cr, P) and infrared analysis.



The highest molecular weight, $CHCl_3$ soluble, fraction thus far obtained had a molecular weight of 7130 (osometric in $CHCl_3$). It appears to have the following structure based on elemental (C, H, P, Cr) and infrared analysis.



The average chain length, based on the molecular weight and above structural assignment corresponds to an n of 8. This polymer is insoluble in water and concentrated HCl, and is soluble in hot chloroform and toluene. It is stable to 360°C. with no apparent visual change.

The scope of this novel synthesis is currently being examined and will be reported at a later date.

The authors wish to thank Dr. H. de Schmertzing for the analytical work and Edward Kelly for laboratory assistance.

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TRANSVERSE FLOW IN EXTRUSION RHEOMETERS

Our studies of the flow behavior of polymer melts have shown that transverse flow occurs to a significant degree in the reservoir of capillary extrusion rheometers. This crossflow pattern has been observed in both constant rate and constant pressure instruments. Such flow is important because it appears to be associated with some of the problems encountered in extrusion processes.

Although circulation of the melt in the vicinity of the capillary entrance has been reported (1,2) to our knowledge there has been no discussion of crossflow in the reservoir at distances well removed from the entry. A number of different experiments illustrate the existence of a crossflow pattern. For example (see Fig. 1), a very small amount of

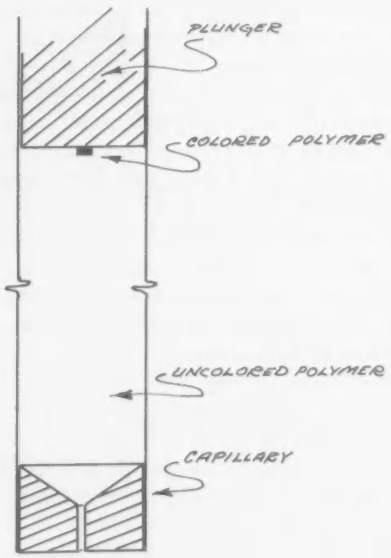

Figure 1.

colored material can be placed on a charge of uncolored polymer (in the reservoir) which is then forced through a capillary. The resulting monofilament will consist of a long uncolored section, a relatively short section containing colored polymer and then another long uncolored section. The relative amounts of colored and uncolored material depend on the

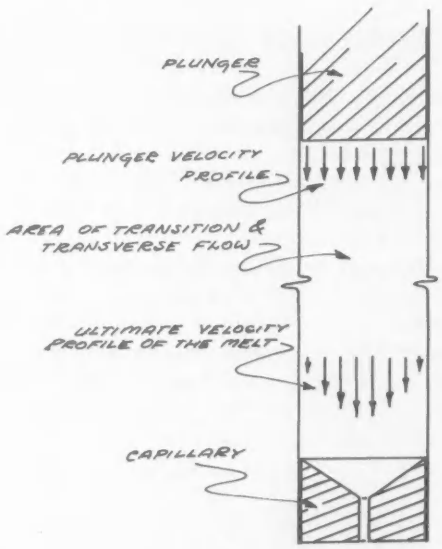

Figure 2.

specific arrangement but it appears that 20–30% of the material in the reservoir participates in the crossflow. It is obvious from the rheometer configuration (see Fig. 2) that transition from a plug velocity profile to a parabolic type velocity profile must be accompanied by transverse flow. However, the magnitude of the crossflow may not have been recognized. There is evidence which suggests that in a multiviscosity system the transverse flow has a profound effect.

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POLYMER LETTERS VOL. 1, PP. 463-464 (1963)

MONOMER REACTIVITY RATIOS FOR THE STYRENE/o-DIVINYLBENZENE COPOLYMERIZATION

We have previously reported (1) reactivity ratios for styrene/m-divinylbenzene ($r_1 = 0.65$; $r_2 = 0.60$) and the lack of a definitive solution of the copolymerization equation for the styrene/p-divinylbenzene copolymerization. It has been pointed out (2) that the copolymerization of these divinyl compounds to low conversion probably involves only one of the vinyl groups of the divinylbenzene and that the high (80%) p-divinylbenzene copolymerization might be discarded as abnormally involving the second vinyl group and thus distorting the analysis. Using the 80/20 and 50/50 (approximately) monomer charge copolymerizations, values of $r_1 = 0.14$ and $r_2 = 0.5$ apply to the styrene/p-divinylbenzene copolymerization.

The availability of o-divinylbenzene (3) has prompted our determination of the reactivity ratios for this monomer to complete the data for the three isomers. Copolymerization was carried out at 80°C. with benzoyl peroxide initiator to give white, powdery solid copolymers which were soluble in benzene. The copolymer composition was decermined by radioactivity assay of its styrene-β-C^{14} content using ionization chambervibrating reed electrometer assay techniques (4) which have previously been used by us (5). The revised copolymer composition equation was used to calculate the reactivity ratios. Solution of the equation by the intersection method gave $r_1 = 0.92$, $r_2 = 1.00$ and the Fineman-Ross method (6) gave $r_1 = 0.94$ and $r_2 = 0.99$.

It is interesting to note that the copolymers produced from the styrene/o-divinylbenzene copolymerization did not show any indication of crosslinking as far as solubility is concerned. During purification the copolymers appeared to be completely soluble in benzene unlike the copolymers from the m- and p-isomers which swell but do not dissolve in benzene. This suggests that the o-divinylbenzene cyclopolymerizes and an attempt to evaluate this possibility has been made on the basis of the infrared characteristics of a copolymer containing approximately 25 mole-% of styrene and 75 mole-% of o-divinylbenzene. This copolymer was plated on a potassium bromide pellet from a 12.9% solution in carbon disulfide. There was 90 and 84% absorption respectively in the 909 and 990 $cm.^{-1}$ region indicating the presence of residual double bonds. Comparison of the ratio of intensity of vinyl to aryl absorption in the infrared spectrum for the styrene/o-divinylbenzene copolymer (90/95 at 909/822 $cm.^{-1}$) with the same ratio (90/83 at 909/750 $cm.^{-1}$) in the spectrum of 5% p-methylstyrene monomer in carbon disulfide indicated that there was less than one vinyl per aromatic ring and thus that cyclo-

polymerization probably occurred to some extent. Absence of appreciable cyclopolymerization may be a result of the low conversion conditions. Alternatively, the second divinyl group may have been so shielded that its further reaction was not readily possible.

The authors gratefully acknowledge support provided under Contract AT-(40-1)-229 between the U. S. Atomic Energy Commission and the University of Louisville for radioactivity assay equipment used in the radioisotope studies.

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(2) The authors wish to thank Dr. Frank R. Mayo for this comment.

(3) The o-divinylbenzene used in this study was furnished by Drs. R. W. Keown, M. A. Smook, and H. E. Schroeder of the Elastomer Chemicals Department of the E. I. du Pont de Nemours and Company, Inc. The authors gratefully acknowledge this assistance. The material as supplied (40% in benzene with stabilizer) was fractionated in a spinning band column just prior to use. An intermediate fraction b.p. 48°/3 mm., having N_D^{25} 1.5747 was used; F. W. Hoover, O. W. Webster, and C. T. Handy, J. Org. Chem., 26, 2234 (1961).

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POLYMER LETTERS VOL. 1, PP. 465-470 (1963)

SOLID STATE POLYMERIZATION OF TRIOXANE BY THE SIMULTANEOUS SUBLIMATION OF MONOMER AND IODINE*

Several reports (1-9) about the solid state polymerization of trioxane have been published, but the method of polymerization catalyzed by iodine in the solid state has not been reported as far as the authors know.

Kargin et al. (10) published an interesting method of polymerization which used the simultaneous condensation of vapors of monomers and inorganic substances on a strongly cooled surface. The authors applied Kargin's method to the system of trioxane and iodine.

That is, commercial trioxane (Eastman Kodak and American Cellanese) is purified by several sublimations at high vacuum and then introduced at the pressure of $10^{-4} - 10^{-5}$ mm. Hg into an ampoule cooled by liquid nitrogen. At the same time, the desired quantity of iodine which is also purified by several vacuum sublimations is introduced into the ampoule. This ampoule containing the mixture produced by the simultaneous sublimation of trioxane and iodine is sealed off and placed into a thermostat of a definite temperature. After being left for a definite time, the ampoule is opened. Then, monomer and iodine are removed by benzene and the undissolved polymer is washed twice with benzene. The inherent viscosity of the obtained polymer is measured in p-chlor-phenol solution (0.1 g./100 ml.) containing 2% of α-pinene by using an Ostwald viscometer at 60°C. It is absolutely necessary to raise the temperature of the ampoule after simultaneous sublimation. No polymerization occurs at a reaction temperature of less than 0°C. and only 6% polymer is obtained by keeping the ampoule at 15°C. for 30 min.

Experimental results are shown in Figures 1-4. As shown in Figures 1 and 2, the polymerization yield increases with time but reaches to the limit relatively quickly. The yield also increases with an increase of temperature and of iodine concentration. Although the inherent viscosity does not change with time, it decreases with an increase of temperature and of iodine concentration as shown in Figures 3 and 4, where inherent viscosity is measured for the polymers which are obtained in 30 min. The temperature of the reaction system is not constant during the polymerization, but as a result of temperature measurements made by a thermistor in the ampoule, it is found that the system reaches to the constant temperature of the thermostat 3–4 min. after the ampoule is placed into the thermostat. Therefore, polymerization rates are obtained from the slope of curves after 4 min. in Figures 1 and 2, and the depend-

*The detailed paper will be published in Bulletin of Chemical Society of Japan.

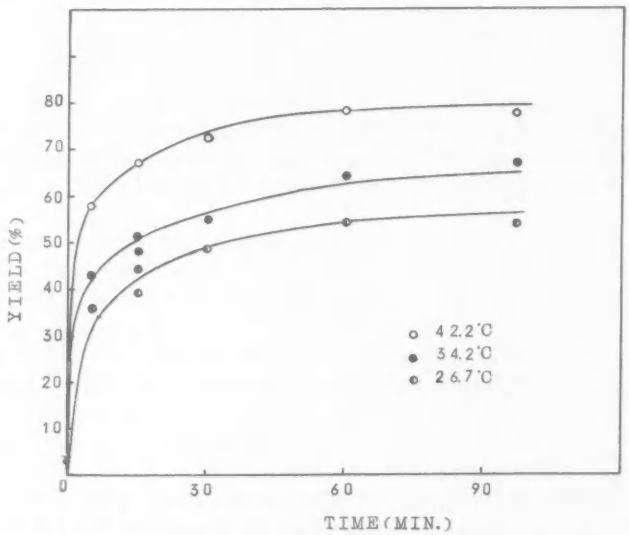

Fig. 1. Change of yield with time at various temperatures. Wt.–% of iodine is 0.67%.

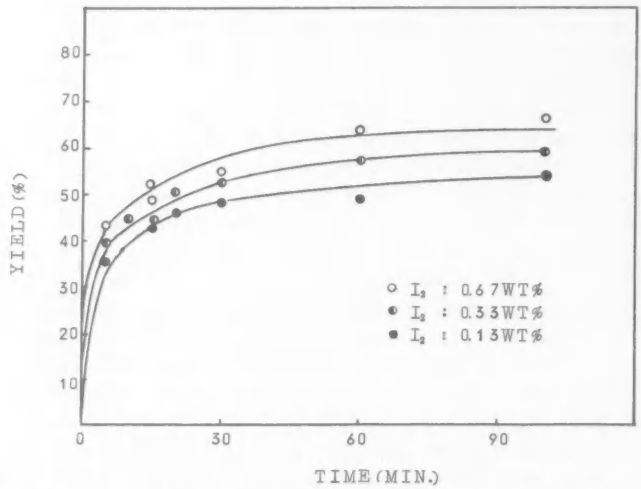

Fig. 2. Change of yield with time at various iodine concentrations at the reaction temperature of 34.2°C.

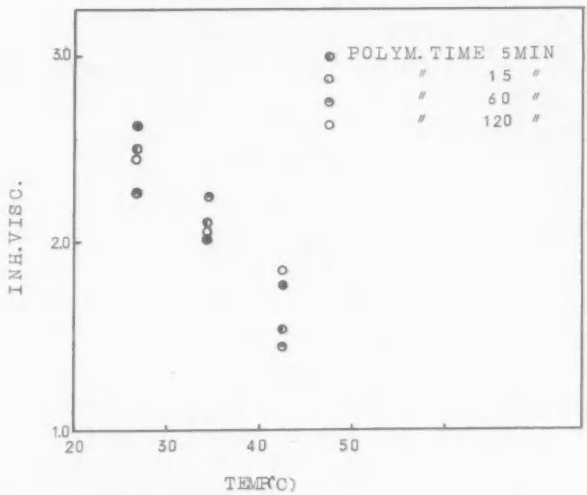

Fig. 3. Change of inherent viscosity with temperature.
Wt.–% of iodine is 0.67.

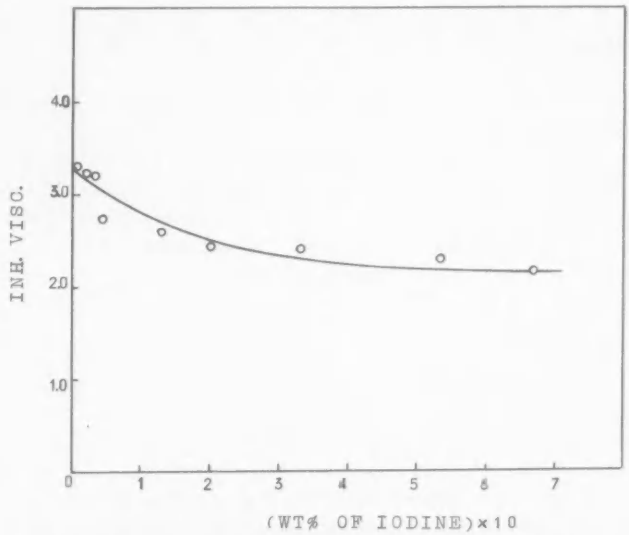

Fig. 4. Change of inherent viscosity with wt.–% of iodine.
Reaction temperature is 34.2°C.

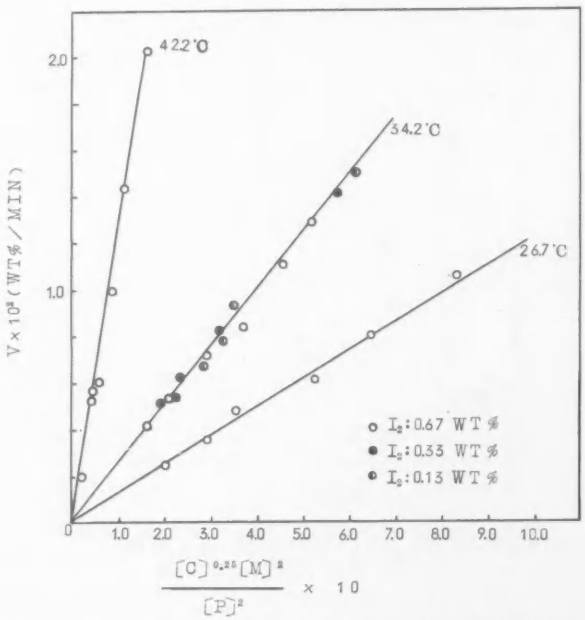

Fig. 5. Change of polymerization rate with $[C]^{0.25}[M]^2/[P]^2$ where [C], [M], and [P] are wt.–% of iodine monomer and polymer, respectively.

ence of these rates upon the concentrations of monomer, iodine, and polymer is examined.

Thus, it is found that the polymerization rate V is proportional to $[C]^{0.25}[M]^2/[P]^2$ as shown in Figure 5, where [M], [C], and [P] are weight percentages of monomer, iodine, and polymer, respectively. From the slope of straight lines of Figure 5, rate constants at various temperatures are obtained for the following equation:

$$V = k[C]^{0.25}[M]^2/[P]^2$$

From Arrehenius' plot of log k vs. 1/T, the activation energy is found to be about 29 Kcal./mole. In order to confirm that the simultaneous sublimation is absolutely necessary, trioxane is placed into the ampoule at first without sublimation and then iodine is sublimed into the ampoule. As shown in Table I, where 0.01 g. of iodine is used for 1.5 g. of trioxane, the method without sublimation of trioxane does not produce polymer of measurable quantity. The reaction time is 15 min. and the reaction temperature is 34.2°C.

TABLE I

Method	Yield, %
Simultaneous sublimation	49.2
Without sublimation of trioxane	trace

Also, it is obvious that the polymerization does not occur in the gas phase because in alternating sublimations, wherein iodine vapor is removed during the sublimation of trioxane and trioxane vapor is removed during the sublimation of iodine, almost the same yield of polymer is obtained, as shown in Table II.

TABLE II

Method	Number of alternating repetitions	Yield, %
Alternating sublimation	2	49.4
	6	52.0
Simultaneous sublimation	–	52.3

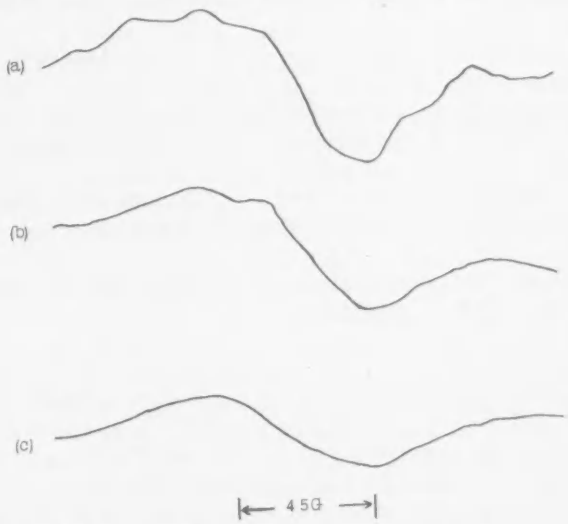

Fig. 6. ESR spectra of reaction mixture. (a) during the polymerization; (b) 10 min. after the ampoule is opened; and (c) 2 days after the ampoule is opened.

In Table II the reaction temperature is 34.2°C., the quantity of iodine is 0.01 g./1.5 g. of trioxane, and the reaction time is 30 min. According to ESR measurements of the reaction system at room temperature, the spectra shown in Figure 6 are obtained. After opening the ampoule, the intensity of spectrum decreases with time. Also, the presence of air, oxygen, and other radical scavengers inhibits this polymerization reaction. From these results, the authors prefer to explain this reaction by assuming that the initiation of radical polymerization takes place in association with crystal dislocations or imperfection caused by simultaneous sublimation and that the propagation step starts somewhere between 0° and 15°C. However, the existence of a radical is not conclusive proof for the radical mechanism, and further study is necessary to explain the detailed mechanism of this reaction.

The authors wish to express their thanks to Dr. K. Kurita and Mr. H. Iguchi for their help in the ESR measurement.

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POLYMER LETTERS VOL. 1, PP. 471-476 (1963)

CRYSTALLINE FORMS OF POLYPENTENE-1

Natta (1) has described a crystalline form of isotactic polypentene-1 with a melting point of 75–80°C., a density of 0.87 g./cc. and a crystalline identity period of 6.60 ± 0.15 A. and a ternary helical chain configuration. A recent communication by Danusso (2) describes the production in the unoriented form of two crystalline forms, Types I and II, and gives volumetric and dilatometric data for both forms.

We also have observed these two basic crystalline forms in both oriented and unoriented specimens and have examined the unit cells and chain configurations of the two forms. Both crystal forms show some variations in their diffraction patterns.

Polypentene-1 was polymerized in these laboratories with a $TiCl_3$ and $Al(Et_2)Cl$ catalyst in a hydrocarbon diluent, and precipitated from the viscous reaction liquid and washed with acetone. Comparison with the x-ray diffraction scans given by Danusso (2) showed that the polymer as prepared was in the form they designate Type I; it was ~40% crystalline. A highly crystalline (>50%) form with diffraction pattern similar but not identical to that of their Type II was formed when the polymer was cooled slowly, at 6°C./hr., from 100–120°C.; this we have designated Type IIa.

Type II Crystalline Form

The small variations observed in the diffraction patterns of the basic Type II form are the result of different heat and mechanical treatments, and are apparent in both oriented and unoriented specimens. The crystal form (Type IIb) obtained on quenching a thin sheet from ~130°C. to low temperatures (–80°C. was actually used) resembles more closely the form shown by Danusso (2). X-ray diffraction scans, obtained with a Philips diffractometer and proportional counter with pulse height discrimination, of Types IIa and IIb are shown in Figure 1.

Well oriented, crystalline, fibers were obtained by drawing fibers from strips of pressed sheet, in a Type II form intermediate between IIa and IIb and free from Type I, at temperatures from 45–80°C. Fibers drawn at 65°C. showed the Type IIa form, and those drawn at 80°C. were less well oriented and showed the Type IIb form. The x-ray patterns, especially that of the 65°C. fiber which is shown in Figure 2a, bear a marked resemblance to that of oriented poly-3-methyl-butene. The chain configuration is a 4_1 helix and the unit cells given below in Table I, which were derived from the diffraction patterns of the 65°C. fiber and the 80°C. fiber, respectively, are slightly different. Both are monoclinic

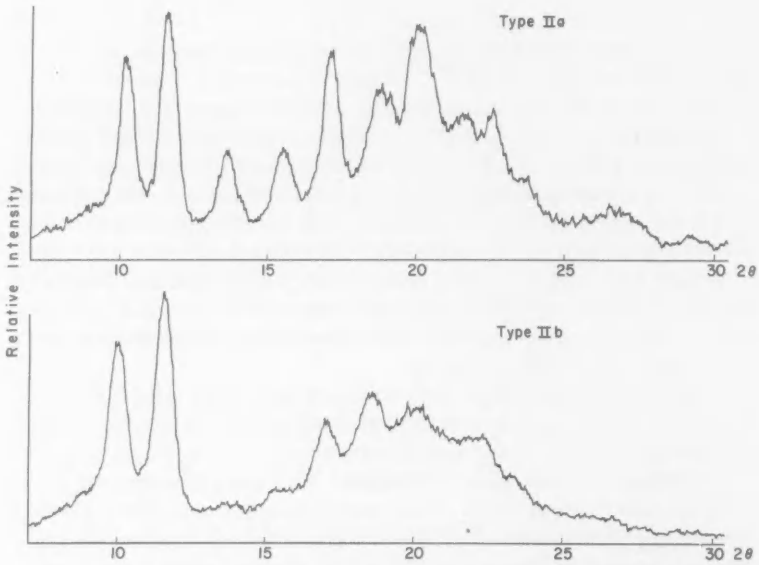
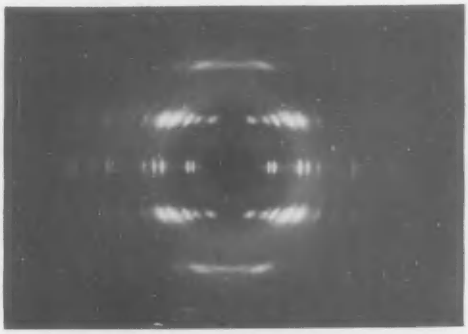


Fig. 1. X-ray diffractometer scans of type IIa and IIb crystalline forms (Cu-K_α radiation).

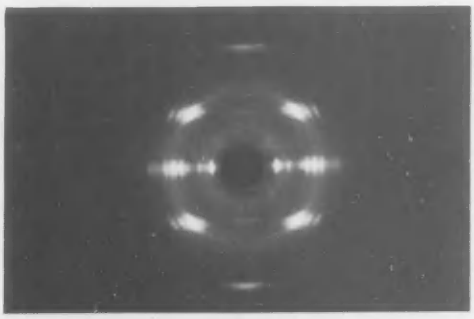
with the c (fiber axis) the unique axis and are pseudo-orthorhombic since (a cos γ = b/2).

The crystalline density is consistent with the observed density of 0.875 g./cc. for a ~50% crystalline specimen. The closely similar pseudo-tetragonal unit cell of poly-3-methylbutene which was originally derived by Natta (3), is given for comparison (we have found that the original cell network requires to be doubled to fit all the observed reflections both on the layer lines and on the equator).

The changes in cell dimensions from the Type IIa to Type IIb form reflect an increasing departure from the true pseudo-tetragonal network (a sin γ = b) shown by poly-3-methylbutene. It is likely that the equatorial cell network may show a continuous small change in dimensions so that the unit cells given above are only two such networks produced by the particular conditions of drawing. When the fiber in the IIb form was heated at 80°C. at constant length the diffraction pattern became closer to that of the IIa form. It seems likely that these small differences in the equatorial unit cell dimensions are associated with small differences in the disposition and packing of the side groups which may vary according to the conditions of crystallization.



(a)



(b)

Fig. 2. X-ray diffraction photographs of fiber orientation in (a) the type IIa crystalline form, (b) the type Ia crystalline form. (Using a 3 cm. camera, Cu-K_α radiation.)

Type I Crystalline Form

Moldings made from the original polymer in the Type I form (Type Ia) by pressing at 100°C. for 5 min. and then quenching to room temperature resulted in only partial conversion to Type II. Highly oriented fibers drawn at 50°C. from this molding showed some well oriented Type IIa and (principally) a well oriented crystal form (Type Ib) resembling Type Ia in the spacings of its strongest reflections, but showing some changes in diffraction pattern, particularly in intensities, from Type Ia. The

TABLE I

Cell Constants of Types IIa and IIb Polypentene-1 and Poly-3-Methylbutene

	Type IIa	Type IIb	Poly-3-methylbutene
a	19.30 A.	19.60 A.	19.25 A.
b	16.90 A.	16.75 A.	17.20 A.
c	7.08 ± 0.05 A.	7.08 ± 0.10 A.	6.85 ± 0.05 A.
γ	116°	115° 20′	116° 30′
a sin γ	17.30 A.	17.75 A.	17.20 A.
Chains/cell	4	4	4
Helix	4_1	4_1	4_1
Crystal density	0.90 g./cc.	0.885 g./cc.	0.92

Type Ib reflections were all rather diffuse and could readily be distinguished from the sharp Type IIa reflections present and they are few in number. The layer lines of the Types Ib and IIa forms were clearly resolved. Type Ib has a fiber repeat of 6.5 A. and the chain configuration is a 3_1 helix.

On heating a fiber showing mixed Type Ib and IIa crystallinity at 80°C. for 16 hr. at constant length well oriented Type Ia crystallinity developed, free from Type II. Thus both Types Ib and IIa convert to Ia on prolonged heating at 80°C. This is consistent with the slow conversion of Type II to Type I at temperatures above 80°C. observed by Danusso (2).

The diffraction pattern of Type Ia is shown in Figure 2b. The repeat unit is 6.49 A. and the chain configuration is a 3_1 helix. All the equatorial reflections fit an orthogonal cell network with

$$a_0 = 11.20 \text{ A.} \qquad b_0 = 20.85 \text{ A.}$$

The only regular absences were h00 (h odd) and 0k0 (k odd). The crystal density is 0.92 g./cc. for four chains per cell. The unit cell is monoclinic but we have not been able to distinguish with certainty between the two cells given below:

a = 11.35 A.	b = 20.85 A.	c = 6.49 A.	β = 99.6°
a = 21.15 A.	b = 11.20 A.	c = 6.49 A.	β = 99.6°

TABLE II

d-Spacings of Types Ia and Ib Crystal Forms

Type Ia				Type Ib		
I	d_{obs} (A.)	Layer line	Index	I	d_{obs} (A.)	Layer line
vs	10.5	0	020	vs	10.5	0
mw	7.7	0	120	? [a]	?	–
mw	6.4	1	–	–	–	–
vw	6.0	0	130	w	6.0	0
vw	5.6	0	200	–	–	–
s	5.43	0	210	w	5.4	0
w	5.06	1	–	mw	5.0	0
ms	4.98	0	220	–	–	–
ms	4.77	0	140	–	–	–
vs	4.67	1	–	vs	4.65	1
ms	4.46	1	–	–	–	–
ms	4.39	0	230	vw	4.40	0
m	4.18	1	–	–	–	–
vw	3.96	0	150	–	–	–
m	3.83	1	–	–	–	–
vw	3.84	0	240	–	–	–
m	3.68	0	310	–	–	–

[a] The strong Type II line present here would mask a Type Ib reflection.

The d-spacings out to 3.68 A. of the observed first and second layer line reflections of the oriented Type Ia form are given in Table II in comparison with the few rather diffuse reflections from Type Ib. It will be seen that the latter fit the Type Ia unit cell but the intensity variations and broadening of the reflections suggest that the packing of the chains is different and is not completely ordered.

The higher density of the Type I form compared with that of Type I is consistent with the former being the more stable form as reported by Danusso (2). Interconversion between the two forms does not take place readily but Type II tends to be converted to Type I on drawing. Cold drawn strips of pressed sheet. originally in the Type II form intermediate

between IIa and IIb, showed highly oriented Type I with very broad reflections, indicating a paracrystalline phase rather than a crystalline phase, together with rather poorly oriented Type II. On heating this fiber at 80°C. for 1 hr., a mixture of well oriented Type Ib and Type II was obtained.

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POLYMER LETTERS VOL. 1, PP. 477-481 (1963)

DIFFUSION CONTROLLED TERMINATION IN FREE RADICAL POLYMERIZATION

Free radical polymerizations of many monomers, for example, methyl methacrylate, are subject to the Trommsdorff effect, wherein the rate and degree of polymerization increase with the extent of reaction. If the excess heat generated by the increased rate is not dissipated, the temperature rises and aggravates the effect. This behavior has been the subject of a number of investigations, particularly by North and co-workers (1-3). Through their efforts it has become rather well-established that the behavior is due to a decrease in the rate of termination of the growing chains caused by the high viscosity of the partially polymerized system.

Unfortunately, it is difficult to develop useful but still quantitative kinetic equations, applicable throughout the course of a polymerization, which embody this concept. Techniques which suppose steady state concentrations of the radical species are inapplicable.

In this communication we should like to suggest a rather simple approach to the effect: one which leads to convenient linear relations between the rate and degree of polymerization and the bulk viscosity. The results are strictly applicable to model systems of the sort described by Atherton and North (3) but may also be used to estimate the rate and degree of polymerization at particular stages at any degree of conversion.

A. System Without Transfer Agent

We suppose that the mutual termination of two growing chains consists of just two steps. The first is a viscosity dependent diffusion of the two chains to one another. The second is a viscosity independent mutual termination.

Consider, then, a polymerizing system in which monomer, M, and initiator, I, are present. The reactions which we allow are as follows:

$$I \xrightarrow{k_d} 2R\cdot \qquad \text{decomposition} \qquad (1)$$

$$R\cdot + M \xrightarrow{k_i} M\cdot \qquad \text{initiation} \qquad (2)$$

$$M_r\cdot + M \xrightarrow{k_p} M_{r+1}\cdot \qquad \text{propagation} \qquad (3)$$

$$M_r\cdot + M_s\cdot \xrightarrow{k_t} P_r + P_s \qquad \text{termination} \qquad (4)$$

The termination step (4) may be split into two parts as described above.

$$M\cdot + M\cdot \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [M:M] \qquad (4a)$$

$$[M:M] \xrightarrow{k_3} 2P \qquad (4b)$$

The symbol [M:M] refers to two growing chains being in such a position that if they have sufficient energy, they can react. Equation (4a) is reversible since the radicals need not react upon coming together.

Applying a steady state condition to [M:M], we find

$$[M:M] = \frac{2k_1 [M\cdot]^2}{k_2 + k_3}$$

and the rate of termination of the chain radicals becomes

$$R_t = \frac{2k_1 k_3}{k_2 + k_3} [M\cdot]^2$$

The rate constants in (4a) are both assumed to be diffusion dependent. Benson and North have suggested that this may be accounted for by assuming that they are both inversely proportional to the bulk viscosity, η (2).

$$k_1 = k'_1/\eta \qquad k_2 = k'_2/\eta$$

where the primed constants are independent of viscosity. Then

$$R_t = \frac{2k'_1 k_3}{k'_2 + k_3\eta} [M\cdot]^2$$

Formal extension of the treatment is difficult for practical systems, but some qualitative remarks may be made. Polymerization in a free radical initiated system must strive toward some equilibrium state where $R_t = R_i$. For it to do so under the conditions we have outlined requires that

$$[M\cdot] \propto \eta^{1/2}$$

The steady increase here will be reflected in both the rate and degree of polymerization.

$$R_p = k_p [M] [M\cdot] \propto \eta^{1/2}$$

$$DP = \frac{R_p}{R_i} \propto \eta^{1/2}$$

The treatment may be applied formally to an experimentally more at-

tractive situation. Suppose polymerizations are carried out in a series of solvents which differ only in viscosity. If there are no complicating factors such as chain transfer to solvent, the kinetic constants are the same as those for an undiluted system at that viscosity. However, steady state concentrations of the radical species may be assumed and expressions for the rate and DP are easily found. They may be put into the following convenient forms.

$$\frac{R_p^2}{k_p^2 [M]^2} = \frac{R_i k'_2}{2k'_1 k_3} + \frac{R_i \eta}{2k'_1} \tag{5}$$

$$\frac{(DP)^2}{k_p^2 [M]^2} = \frac{k'_2}{2R_i k'_1 k_3} + \frac{\eta}{2R_i k'_1} \tag{6}$$

Atherton and North have recently published data for experiments of the type outlined above (3). From their results we plot R_p^2 and $[\eta]^{8/3}$, which is roughly proportional to $(DP)^2$, against the solvent viscosity. Within experimental error, straight lines result (see Figs. 1 and 2). From the lines a number of the rate constant combinations can be determined. For example, we find for methyl methacrylate

$$k'_2/k_3 = .16 \text{ poise}; \quad R_i/k'_1 = 9.6 \times 10^{-18} \text{ moles}^2 \text{ poise}^{-1}$$

with (3) $k_p = 229$ mole^{-1} sec.$^{-1}$. The relations apparently hold even for the copolymerization reaction although it was not explicitly considered.

For the undiluted system, then, the constants could be used to calculate R_p and DP at any stage of a polymerization for which the viscosity is known.

In this treatment the dependence of the rate constants in (4a) have been assumed independent of chain length. Certainly this cannot be true. To include such an effect would not substantially alter our conclusions but would, in addition, predict broader molecular weight distributions.

B. Effect of Chain Transfer

Intuitively, we would expect that a chain transfer agent would exert a moderating influence on the Trommsdorff effect. First, the production of lower molecular weight polymer would result in a lower bulk viscosity at a given conversion, thereby decreasing the autoacceleration at that conversion. Second, if most chains are terminated by chain transfer, the Trommsdorff effect would be damped, since the transfer reaction should not be as viscosity dependent as the mutual termination of long chains.

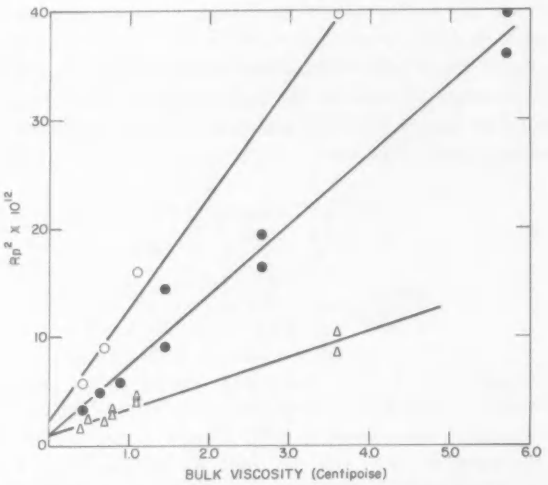

Fig. 1. Bulk viscosity dependence of rate of polymerization: (●) methyl methacrylate, (○) vinyl acetate, (Δ) copolymer.

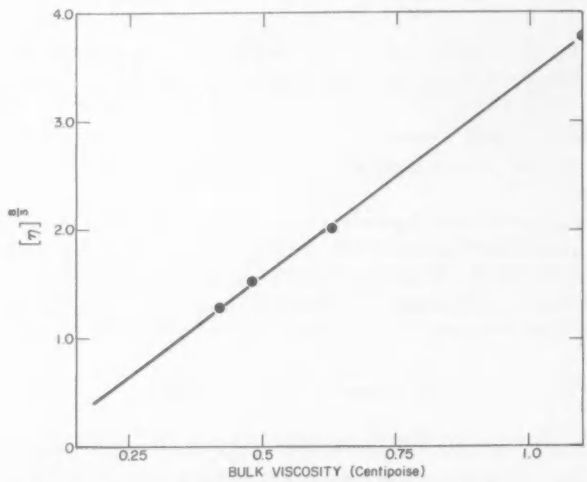

Fig. 2. Bulk viscosity dependence of copolymer molecular weight. $[\eta]$ is assumed proportional to $M^{0.75}$.

Let us examine these assertions quantitatively. Suppose that in addition to reactions (1-4), the following may occur.

$$M_r^{\bullet} + T \xrightarrow{k_{tr}} P_r + T^{\bullet} \qquad (7)$$

$$T\cdot + M \xrightarrow{k'_1} M\cdot \tag{8}$$

In this case the rate of termination becomes,

$$R_t = \frac{2k'_1k_3}{k'_2+k_3\eta}\,[M\cdot]^2 + k_{tr}\,[T]\,[M\cdot]$$

where once again the importance of the viscosity of the medium is apparent. There is, as before, a conceptual advantage in considering the model system wherein we may apply steady state kinetics. Expressions for R_p and DP are easily developed.

$$\frac{R_p{}^2}{k_p{}^2B\,[M]^2} = \frac{k'_2}{2k'_1k_3} + \frac{\eta}{2k'_1} \tag{9}$$

and

$$\frac{1}{DP} = \frac{B^{1/2}}{k_p\,[M]\,\dfrac{k'_2}{2k'_1k_3} + \dfrac{\eta^{1/2}}{2k'_1}} + \frac{k_{tr}\,[T]}{k_p\,[M]} \tag{10}$$

where $B = 2\,k_d f\,[I]$.

These equations generally support the assertions made above. When most of the chains are terminated by transfer, DP will be virtually unaffected by viscosity since the second term of eq. (10) will dominate at all viscosities. For a bulk polymerization, by keeping the molecular weight low and controlling it, the viscosity at a given percent conversion will be lower than for the corresponding system without transfer agent. R_p will then increase at a far lower rate as the polymerization proceeds.

Equations 9 and 10 could be tested by using a system similar as Atherton and North's but which would include a transfer agent.

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POLYMER LETTERS VOL. 1, PP. 483-488 (1963)

Co^{60} γ-RAY INDUCED COPOLYMERIZATION OF ETHYLENE IN THE PRESENCE OF OTHER MONOMERS*

Very little has yet been reported on the radiation-induced copolymerization of ethylene with other monomers.

The experimental approach was to determine if copolymerization of the various systems occur in a radiation field, and to investigate some of the properties of the resulting polymers.

Experimental

The ethylene gas was supplied by Phillips Petroleum Co. and had a concentration of 99.9% with <5 ppm 0_2.

The inhibitors present in the liquid monomers were removed by distillation under reduced pressure. Inhibitors present in the gaseous monomers were usually nonvolatile and no attempt was made to remove them from the monomers.

A high pressure reaction vessel of 316 stainless steel having an o.d. of 2 in., and i.d. of 1 in., and a length of 10 in. was used for conducting the copolymerization experiments. Measured amounts of comonomers were introduced into the reaction vessel through a vacuum system. Ethylene gas was fed into the vessel through a compressor to a total pressure of $\approx$ 10,000 psi.

After charging, the vessel was exposed to radiation in the gamma pool facility at Brookhaven National Laboratory without agitation.

The copolymers were isolated from unreacted monomers and homopolymers by the preferential solvent extraction method and the fractional precipitation method, as shown in Figure 1. The presence of the true copolymers was established by IR spectra.

To determine solubilities of the isolated copolymers a 1% mixture of polymer with solvent was used. Table I shows some of the solubility characteristics of the isolated copolymers in various solvents.

Copolymer film made by hot-pressing powdered samples with a Carver Press were used for density measurements by the gradient tube technique and for infrared examination. The composition of the copolymer was determined, whenever possible, by elemental analysis.

The presence of crystallites and subsequently the crystalline melting points, shown in Table II, were determined by noting the disappearance of birefringence observed between crossed polarizers on a hot-stage polarizing microscope.

*Work performed under the auspices of the U. S. Atomic Energy Commission, Division of Isotope Development.

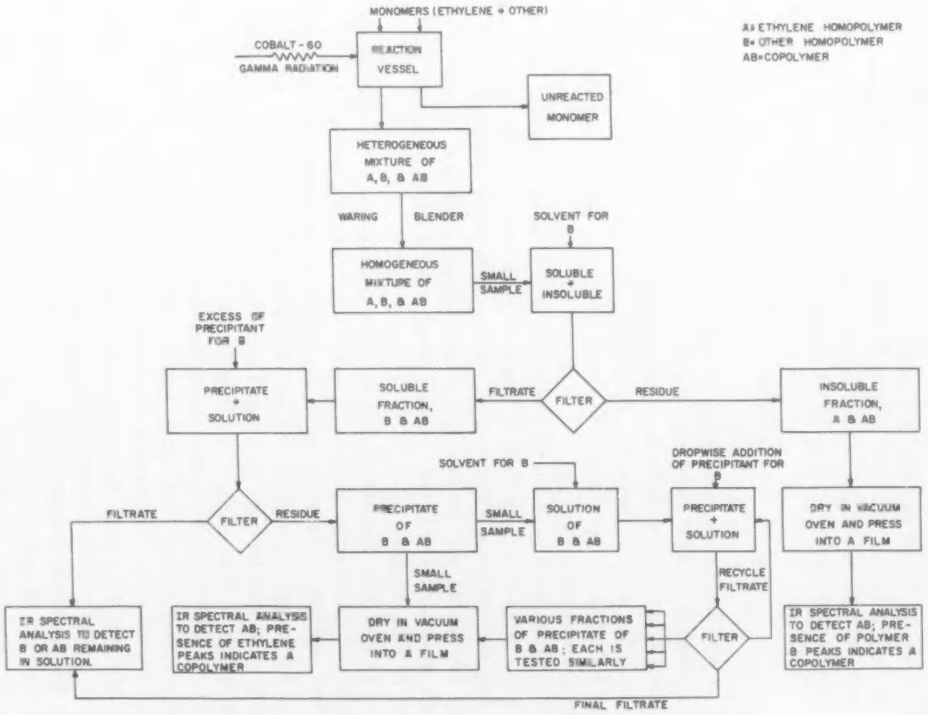
MONOMERS (ETHYLENE + OTHER)
A= ETHYLENE HOMOPOLYMER
B= OTHER HOMOPOLYMER
AB=COPOLYMER
COBALT-60
GAMMA RADIATION
REACTION VESSEL
UNREACTED MONOMER
HETEROGENEOUS MIXTURE OF A, B, & AB
WARING BLENDER
SOLVENT FOR B
HOMOGENEOUS MIXTURE OF A, B, & AB
SMALL SAMPLE
SOLUBLE + INSOLUBLE
EXCESS OF PRECIPITANT FOR B
PRECIPITATE + SOLUTION
SOLUBLE FRACTION, B & AB
FILTRATE
FILTER
RESIDUE
INSOLUBLE FRACTION, A & AB
SOLVENT FOR B
DROPWISE ADDITION OF PRECIPITANT FOR B
FILTRATE
FILTER
RESIDUE
PRECIPITATE OF B & AB
SMALL SAMPLE
SOLUTION OF B & AB
PRECIPITATE + SOLUTION
DRY IN VACUUM OVEN AND PRESS INTO A FILM
SMALL SAMPLE
RECYCLE FILTRATE
IR SPECTRAL ANALYSIS TO DETECT B OR AB REMAINING IN SOLUTION.
IR SPECTRAL ANALYSIS TO DETECT AB; PRESENCE OF ETHYLENE PEAKS INDICATES A COPOLYMER
DRY IN VACUUM OVEN AND PRESS INTO A FILM
VARIOUS FRACTIONS OF PRECIPITATE OF B & AB; EACH IS TESTED SIMILARLY
FILTER
IR SPECTRAL ANALYSIS TO DETECT AB; PRESENCE OF POLYMER B PEAKS INDICATES A COPOLYMER
FINAL FILTRATE

Fig. 1. Scheme for identification and isolation of copolymers.

TABLE I

Solubilities of Ethylene Copolymers

Ethylene copolymer	Decalin	Dioxane	Benzene	Carbon tetra-chloride	Dimethyl formamide	Ethyl acetate	Tetra-hydrofuran	Xylene	Cyclo-hexane	Heptane
Styrene	S [a]	S	S	–	–	–	–	–	–	–
Divinyl benzene	I	I	I	I [e]	–	I	–	I	–	I
Methyl methacrylate	S* [b]	S	PS* [d]	S*	–	I	–	S*	–	–
Methyl acrylate	S	I	PS*	I	–	I	–	S	–	–
Vinyl acetate	S	S*	S	S	–	PS*	S*	S	–	–
Allyl acetate	I	I	I	I	–	I	–	I	–	PS*
Isobutylene	S	–	S	S	–	–	–	S	S*	–
trans-2-Butene	S	I	S	S	–	I	–	S	–	–
cis-2-Butene	S	–	I	S*	S	–	–	S*	I	PS*
1-Butene	S*	–	I	S*	–	–	–	S*	S*	–
Isoprene	–	–	I	I	–	–	–	I	–	S*
Propylene	S	S	PS	S	–	S*	–	S*	–	S*
Acrylonitrile	I	–	–	–	S	–	I	I	I	–
Chlorotrifluoroethylene	S*	I	–	S*	–	–	PS*	S*	S*	–
Vinyl chloride	S	PS [c]	S	S*	–	S*	S	S	PS*	I
Carbon monoxide	I	I	S	I	I	–	–	S	–	–
Vinyl pyrollidone	PS*	I	PS	PS*	–	I	–	S	–	–
Methyl vinyl ketone	I	–	I	S*	–	I	–	I	I	–

[a] S, Soluble at room temperature.
[b] S*, Soluble at elevated temperatures.
[c] PS, Partially soluble at room temperature.
[d] PS*, Partially soluble at elevated temperatures.
[e] I, Insoluble.

TABLE II

Co^{60} Gamma Copolymerization of Ethylene

Copolymer	Copolymer Characteristics				
	Mole ratio ethylene / comonomer	Mole ratio polyethylene / copolymer	Density, g./cc.	Crystalline melting point, °C.	Molecular weight, $\bar{M}_w$
Styrene	7.4	–	1.000	Noncryst.	–
Divinyl benzene	21.2	–	–	–	–
Methyl methacrylate	17.5	3.6	0.956	125	530,000
Methyl acrylate	31.6	2.2	0.955	123-126.5	–
Vinyl acetate	5.5	7.1	0.963	105-106.5	–
Allyl acetate	6.5	93.2	0.939	122	–
Isobutylene	9.0	–	0.908	103-107.5	–
trans-2-Butene	8.2	–	0.954	103-107.5	190,000
cis-2-Butene	6.7	–	0.963	125-126	–
1-Butene	10.8	–	0.912	102	–
Isoprene	18.7	–	0.956	122	–
Propylene	5.5	–	0.910	95	67,000
Acrylonitrile	3.8	0.24	1.120	Noncryst.	–
Chlorotrifluoroethylene	28.0	13.2	1.004	122	250,000
Vinyl chloride	7.3	1.3	–	Noncryst.	–
Carbon monoxide	7.9	1.95	1.090	112.5	–
Vinyl pyrollidone	14.4	27.7	1.008	120.5	450,000
Methyl vinyl ketone	10.9	51.7	0.942	125	–

TABLE III

Co^{60} Gamma Copolymerization of Ethylene[a]

Comonomer	Intensity, rads/hr.	Total dose, 10^6 rad	Ethylene, g.	Comonomer, g.	Total polymer formed, g.	Total conversion, Wt.-%	G_{Total}
Styrene	132,000	9.0	43.2	21.7	–	–	–
Divinyl benzene	230,000	16.0	47.4	10.4	8.4	14.5	–
Methyl methacrylate	111,000	2.9	49.0	10.0	23.3	39.5	3,000
Methyl acrylate	200,000	5.5	51.2	5.0	15.3	27.2	1,000
Vinyl acetate	308,000	0.92	41.5	23.3	22.3	34.4	10,200
Allyl acetate	308,000	0.92	41.9	22.9	24.8	38.3	13,800
Isobutylene	230,000	0.92	44.5	13.4	1.4	2.4	–
trans-2-Butene	200,000	10.0	45.4	10.7	9.9	17.6	–
cis-2-Butene	308,000	0.92	44.8	13.3	4.2	7.2	–
1-Butene	230,000	0.92	46.5	8.3	4.5	8.2	–
Isoprene	308,000	0.92	49.3	6.4	1.6	2.9	–
Propylene	200,000	14.7	43.1	11.8	43.1	78.5	–
Acrylonitrile	230,000	0.92	41.9	20.9	17.2	27.4	5,900
Chlorotrifluoroethylene	216,000	0.5	49.0	7.3	20.0	35.5	20,000
Vinyl chloride	308,000	0.92	47.4	14.4	5.9	9.5	7,600
Carbon monoxide	230,000	11.0	48.3	6.1	11.2	20.6	640
Vinyl pyrollidone	230,000	16.3	45.5	12.5	54.0	93.1	1,750
Methyl vinyl ketone	308,000	14.4	47.6	10.9	22.4	38.3	890

[a]Irradiation conditions and yields at 20°C.

Several weight average molecular weight measurements were made by the light scattering method. The measurements were determined for soluble material obtained at room temperature.

Because of the high vapor pressures of the monomers used, the experiments were conducted in two-phase systems with the exception of the ethylene-carbon monoxide system. With this procedure, the concentration of monomers varied from the bottom to the top of the vessel. High total doses were given each system to allow for the maximum opportunity to react, and also to produce sufficient material for physical and chemical tests.

Discussion and Results

In the copolymer systems, shown in Table III, the reaction products were free of homopolymer except for the systems with vinyl acetate, vinyl chloride and acrylonitrile. This was probably due to the large radiation dose received by these systems resulting in the depletion of the comonomers.

Ethylene gas can react with a variety of monomeric materials to form copolymers at low temperatures and moderate pressures. The ability for reactions to take place at low temperatures makes it possible to copolymerize monomers which are very sensitive to the elevated temperatures required by conventional free radical catalytic methods.

Unsaturated monomers, such as propylene and the butenes, which do not readily homopolymerize in a radiation field, or by a free radical mechanism can be copolymerized with ethylene by gamma radiation.

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POLYDISPERSITY INDEX HAVING PARTICULAR APPLICABILITY TO NARROW MOLECULAR WEIGHT DISTRIBUTION POLYMERS

It has been common practice to indicate the sharpness of the molecular weight distribution of polymers by the ratio of weight average to number average molecular weight, $<MW>_w/<MW>_n$, which is identical to the ratio of weight average to number average degree of polymerization $<DP>_w/<DP>_n$. This has been used increasingly often in recent years since the advent of the anionic polymerizations which should theoretically yield polymers having Poisson distributions of degree of polymerization.

Note: It is meaningless to speak of a Poisson distribution of molecular weight. The Poisson distribution is a probability distribution; hence it applies only to numbers of events rather than to physical quantities as may be the case with a statistical distribution. This may seem a triviality, but it takes on significance when one considers that the variance of a Poisson distribution is identical to the mean of the same distribution. In a statistical distribution of a physical quantity, the dimension of the variance is the square of the dimension of the mean, which could be true for the Poisson distribution only if the mean and variance are a pure number.

I should like to propose the use of the function

$$\Delta = \left[\frac{<MW>_w}{<MW>_n} - 1\right]^{1/2} = \left[\frac{<DP>_w}{<DP>_n} - 1\right]^{1/2}$$

as an index of polydispersity which is easier to interpret than the simple ratio.

The significance of Δ can be seen in the following manner. By definition, $<DP>_n = <DP>$ and $<DP>_w = <DP^2>/<DP>$, so that $<DP>_w/<DP>_n = <DP^2>/<DP>^2$ and $\Delta^2 = (<DP^2> - <DP>^2)/<DP>^2$. But the numerator of this expression is the variance of the degree of polymerization. Then Δ is simply the ratio of the standard deviation of the DP distribution to the number average DP.

Both whole polymer samples possessing a (presumably) Poisson distribution of DP and polymer fractions have distributions closely approximating the normal (Gaussian) curve. Then we can say that for such polymers, approximately two-thirds of the molecules have DP within the range $<DP>_n \pm \Delta <DP>_n$. To see how this applies in actual cases, we show some results reported by various workers for narrow distribution polystyrene (PS) and poly-α-methylstyrene (PAMS) in Table I.

TABLE I

Some Examples of Polydispersity Reported Previously

Polymer	$\frac{<DP>_w}{<DP>_n}$	Δ	Reference
PS	1.06	.245	1
PS	1.12	.346	1
PS	1.17	.412	2
PAMS	1.03	.173	3
PAMS	1.05	.224	3
PAMS	1.06	.245	3

If these polymers were truly represented by the Poisson distribution, Δ would be equal to $<DP>^{-1/2}$. Since the polymers referred to in Table I had $<DP>$ of the order of 10^3, the value of Δ should be about .03, and $<DP>_w/<DP>_n$ would be about 1.001.

The major difficulty with $<DP>_w/<DP>_n$ is that it has a value of 1 for perfectly monodisperse polymer and a value in the range of 1.5-2.0 for a linear free radical-initiated vinyl polymer. Thus, a number less than 1.1 appears to indicate very narrow distribution on this scale. However, when put on the Δ scale, it is seen that a ratio of 1.1 indicates that the standard deviation of the distribution is of the order of 30% of the number average of the distribution, which is a far cry indeed from the 3% expected for a Poisson distribution.

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ION-EXCHANGE MEMBRANES BASED ON RUBBER

There have been many attempts in recent years to get ion-exchange materials in the form of thin sheets with good mechanical strength and electro-chemical properties for use as membranes in the electrodialysis of brackish waters. Membranes based on collodion have been studied thoroughly by Sollner and co-workers (1) and though high capacity membranes have been obtained, their use in electrodialysis has been limited because of low mechanical strength. Recent advances (2) in the field are so rapid, that for convenience of discussion, membranes can be divided into (a) homogeneous membranes and (b) heterogeneous membranes.

Homogeneous membranes are prepared by introducing exchangeable groups into a film-forming polymer, e.g., chlorine contained in poly (vinyl chloride) (3) can be converted to an amino group by reacting with a polyalkylene polyamine. Membranes of this type have been prepared from copolymers of styrene and butadiene (4), ethyl acrylate (5), and polyethylene (6) Although good ion-exchange films are obtained by this method, often their mechanical properties are not of the required degree. The reasons for their poor mechanical properties are the drastic conditions required to introduce exchangeable groups, such as SO_3H.

Heterogeneous membranes are those prepared by the mixing of an ion-exchange resin in a fine powder form with a suitable plastic binder, so as to get a uniform dispersion of the resin in the binder. Many commercial units for electrodialysis employ this type of membrane, because by adjustment of the binder-resin ratio, any required mechanical strength may be attained. Also, by use of reinforcing agents, such as carbon black (5), the membrane can be strengthened or it can be made more flexible by using a suitable plasticizer. Concerning the electro-chemical properties of the membranes, it is necessary to study the binder-resin ratio for each type of resin and binder to arrive at an optimum condition for good mechanical strength accompanied by good permselective properties. Polystyrene (6), polymethyl methacrylate (6), polyethylene (5), and polyvinyl chloride (7) have been used as binders to obtain membranes of this type.

Another possible method to increase the mechanical properties is to support the weak membrane by means of a fine screen of nylon (8), Dynel (9), or Saran (10). Such membranes are now commercially available and are in use at various pilot plant units for the electrodialysis of brackish waters (11).

Elastomeric materials have been used (4,5) to make homogeneous membranes. Rubber possesses certain advantages over other binding materials so far used. First, it is not brittle at ordinary temperature. It can

withstand varying stresses owing to its elastic nature. Also, it is very resistant to mild acids, alkalies, and concentrated salt solutions, which are normally used in contact with ion-exchange materials. Due to low permeability characteristics, it can retain a certain amount of moisture for a long time, which is a desirable property in membranes. In view of these advantageous properties, rubber was tried as a binder for the preparation of ion-exchange membranes.

Experimental

Both cation and anion-exchange membranes were prepared from resins prepared in the Laboratory. (a) Cation-exchange resin was obtained from cashew nut shell liquid, formaldehyde, and sulfuric acid (12). (b) Anion-exchange resin was obtained from melamine, formaldehyde, and hexamine (13).

Three methods of fabrication were employed: (a) casting a mixture of the resin dispersion and latex (14), (b) milling together of pale crepe rubber with the resin and sheeting of the product, and (c) molding together of Saran with a mixture of rubber and resin.

Casting. Latex (60% dry rubber content) was stabilized by adding few cc.'s of a 5% solution of Vulcstab L. W.* Na or Cl form of the cation exchange and anion exchange resin was taken in the form of a fine 50% dispersion in water using Darvan No. 1† as dispersing agent. Then, to this dispersion, stabilized latex was added and thoroughly mixed.

The above mixture was poured on a levelled glass plate placed in an oven maintained at 105°C. The edges of the glass plate were raised with Plasticine to act as boundary for the poured liquid resin mixture. The entire assembly was cured for 3½ hr. During the last 30 min., the plate was kept reversed in order to ensure uniform curing on both the surfaces. After curing, the plate and the contents were cooled and then the membrane was peeled out under water. After washing, the membranes were regenerated with 5% hydrochloric acid (for cation-exchange membrane) and 4% sodium hydroxide (for anion-exchange membrane).

Milling. Pale crepe rubber was degraded on a 12 in. laboratory mill for 4 to 6 min. Finely ground (about 200 mesh) resin was added and thoroughly mixed on the roll. Thin sheets were taken out from the mill, hydrated, and regenerated as before.

Reinforcing of the Membranes. As the physical properties, especially tensile strength, were not realized by the above two techniques by using rubber alone as the binder, the above mixtures of rubber and resin were supported with Saran (copolymer of polyvinylidine chloride with polyvinyl chloride) net. Reinforcement was carried out as follows:

A sheet was obtained by milling as above and was cut into a conven-

*I.C.I. stabilizer for Latex.

†I.C.I. dispersing agent.

ient size and the same size of Saran net was placed on it. The surface of the sheet exposed towards the mold was smeared with talcum powder or zinc stearate. The assembly was pressed in a hydraulic press at 55-60°C. for 5 to 6 min. at 400 psi. The membrane was taken out of the mold, hydrated, and regenerated. Membranes obtained by all three methods were evaluated in the following manner:

(a) Capacity. The exchange capacities were determined for the cation-exchange membrane by equilibrating a known weight of the sample in N-sodium chloride solution and for the anion-exchange membrane by equilibrating with N/10 HCl solution under identical conditions. Knowing the moisture content, the capacities on dry basis were calculated.

(b) Resistance. A strip of sodium or chloride form of membrane (6.9 × 1.0 × 0.08 cm.) sample under study was conditioned with N/5 potassium chloride solution. Then the membrane was taken out and the excess of electrolyte was wiped off with a clean filter paper. It was then clamped between two copper terminals of the same width as that of the membrane under test on a perspex bridge. The resistance between the terminals was measured by means of an ohm-meter and the conductivity calculated.

(c) Transport Number. A small circular sample of the membrane, 1.0 in. diameter, was completely converted to potassium or chloride form by washing with an excess of potassium chloride or hydrochloric acid. For transport number determination, two solutions differing in concentration by a factor of 2 were employed. The sample was kept overnight in the electrolyte solution of higher concentration.

The equilibrated sample was clamped between two half cells with a rubber gasket in between to assure leakproof clamping. The two half cells were filled with the solution. The voltage set up between half cells was balanced on a Student potentiometer. A mirror galvanometer with lamp and scale arrangement was used as a null indicator.

Results

The properties of the membranes obtained by all the three methods are given in Table I. The effect of varying rubber contents is shown in Table II.

Conclusions

1. The results presented in the tables tend to show that it would be possible to employ rubber as a suitable base for preparing ion-exchange membranes, adopting different techniques.

2. The physico-chemical properties exhibited by the membranes tend to recommend their adaptability for use in electrodialysis cells and further work in this direction is under progress.

TABLE I

Composition	Capacity, meq./g. (dry)	Tensile strength, lb./sq. in.	Conductivity, Mhos./cm.	Transport number, KCl solution
		Casting		
Latex-CNSL resin	0.82	185	1.98×10^{-3}	t + 0.93
Latex-melamine formaldehyde resin	1.16	175	2.15×10^{-3}	t − 0.72
		Milling (unsupported)		
Pale crepe-CNSL resin	0.85	125	3×10^{-3}	t + 0.94
Pale crepe-melamine formaldehyde resin	1.72	89	1.3×10^{-3}	t − 0.72
		Milling (supported with Saran)		
Pale crepe-CNSL resin	0.56	1080	3×10^{-3}	t + 0.93
Pale crepe-melamine formaldehyde resin	1.40	900	1.01×10^{-3}	t − 0.72

TABLE II

Effect of Varying Rubber Contents

Pale crepe rubber/100 parts of resin	Specific conductivity in Mhos/cm.	
	CNSL resin	Melamine formaldehyde resin [a]
20	3×10^{-3}	1.015×10^{-3}
25	2.7×10^{-3}	0.7968×10^{-3}
30	1.586×10^{-3}	0.4963×10^{-3}
35	1.109×10^{-3}	0.3286×10^{-3}

[a] Vulcanized with sulfur and activators for 30 min. at 120°C.

3. The elastic properties of rubber combined with some of the chemical properties make it an ideal choice for preparing ion-exchange membranes. Other aspects, such as the effect of storage on capacity and permselectivity, and the effect of the rubber-resin combination during milling operation, are under study and will be reported subsequently.

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ON THE STEREOREGULATION IN POLYMERIZATION OF VINYL FORMATE

Previously we (1,2) disclosed that poly(vinyl alcohol) (PVA) derived from vinyl formate has a smaller 1,2-glycol content and is more stereoregular than PVA derived from vinyl acetate where the stereoregularity of PVA was judged from the swelling degree in water (3) and the color reaction with iodine (4). A syndiotactic structure was proposed for the PVA from an x-ray examination of the original poly(vinyl formate) (5), and conclusive evidence for this assumption was presented (6). Lately, researchers of the Diamond Alkali Company (7) have made an observation very similar to our earlier works (1,2,5), and they have emphasized the greater influence of electrostatic over steric effects on controlling polymer regularity in the free radical polymerization of vinyl formate. Stereoregulation in the polymerization of vinyl formate, however, could not be fully interpreted only with these two effects; e.g., as compared with the stereoregulation in the polymerization of vinyl chloroacetate, the stereoregulation in vinyl formate is far more remarkable than that expected from the above two effects. We believe that the interaction between formyl groups of vinyl formate also plays an important role on stereoregulation.

The polymerization medium should have a remarkable influence on stereoregulation provided any association of the monomer occurs. Experimental results clearly show that the polymerization of vinyl formate is such a case in point. Crystallizability of poly(vinyl formate) is strongly affected by the polymerization medium. Moreover, tail-to-tail addition – the 1,2-glycol content of PVA derived therefrom – is also proved to be sensitive to the polymerization medium as given in Table I. In the polymerization of vinyl acetate, the 1,2-glycol content of derived PVA is little affected by the polymerization medium (8).

Imai and Matsumoto (6) disclosed that polymerization media for vinyl acetate can be classified into three groups in relation to stereoregulation: the first group gives polymers more stereoregular than the polymer obtained by bulk polymerization, the second has little effect on stereoregulation, and the third gives polymers less stereoregular than the polymer obtained by bulk polymerization. In vinyl formate, however, bulk polymerization gives the most stereoregularity and the least 1,2-glycol containing polymer at a given temperature. Most of the media belongs to the third group and the rest to the second. As the polarity of the medium increases, the tail-to-tail unit increases and the syndiotactic content decreases in the resulting polymer.

All data described above support the view of monomer association.

TABLE I

Effect of Polymerization Medium on 1,2-Glycol Content of PVA Derived from Vinyl Formate (Polymerization Temp., 30°C.)

Medium, 30 wt.-%	1,2-Glycol content, mole-%
(Bulk)	0.89
Methyl formate	0.92
Methanol	0.93
Acetone	0.94
Ethyl acetate	0.95
Acetonitrile	0.96
Dimethyl sulfoxide	0.97

The association may be based upon a hydrogen bond between formyl groups in the monomer. As for the interaction of this kind, association of methyl formate is deduced by Wilmshurrst from infrared spectral data (9). Strong interaction between formyl groups may also be a cause of the crystallizability of poly(vinyl formate) and of the gelation of poly-(vinyl formate) solutions. Though the form of the association has to be further studied from a physicochemical viewpoint, the monomer association undoubtedly plays an important role on stereoregulation in the polymerization of vinyl formate.

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LOCAL VISCOSITY OF POLYMER MELTS BY PULSED NMR I. POLYETHYLENE GLYCOL

During the course of a high-resolution NMR study of polymers, the present authors encountered the fact that the line width of absorption spectrum, which is the measure of molecular motion, is not always decided by the viscosity, but by another factor; namely, molecular weight. For example, the fluent aqueous solution of polyvinyl alcohol gives a rather broad spectrum, while viscous liquid of pentane-2,4-diol, which is the model compound of the polymer gives a highly resolved spectrum (1). Since the absorption spectrum is narrowed by the motion of a comparatively small scale where the magnetic dipole-dipole interaction affects, previous experimental fact shows that the polymer with large molecular weight does not take rapid micro-Brownian motion, even if it is fluent, and vice versa. This short note is devoted to study such micro-Brownian motion of polymers.

The spin-spin interaction time, T_2, of polyethylene glycol was measured together with the reference specimens by a Japan Electron Optics Laboratory Spin Echo Set (Model JSE-3) operating at 30 Mc/sec. For the convenience of comparison, the adiabatic contribution to T_2, say T_2^*, from the methylenic protons in each sample was determined by high-resolution NMR technique by a Varian Associates High-Resolution NMR Spectrometer (Model V-4311) operating at 60 Mc/sec. The samples used were commercial products representing three kinds of polyethylene glycol whose labelled molecular weights were 400, 1500, and 4000, respectively, ethylene glycol, diethylene glycol, and triethylene glycol.

The obtained T_2's and T_2^*'s at 295 and 323°K. are plotted in Figure 1 as functions of the degree of polymerization, n. Experimental formulas are given from Figure 1 as follows:

$$\begin{aligned} 1/T_2 &= 12.0\, n^{0.2}\ (\text{sec.}^{-1}) \text{ at } 295°\text{K}, \\ 1/T_2 &= 7.7\, n^{0.2}\ (\text{sec.}^{-1}) \text{ at } 323°\text{K}, \\ 1/T_2^* &= 3.4\, n^{0.2}\ (\text{sec.}^{-1}) \text{ at } 295°\text{K}. \end{aligned} \tag{1}$$

Provided that the lattice system is extremely fluctuating (2), $1/T_2$ is given by

$$1/T_2 \doteqdot \sigma^2 \tau_c \tag{2}$$

where σ^2 is the total second moment, which includes non-adiabatic contribution, in sec.^{-2}, and τ_c is the correlation time. Then, the experimentally obtained T_2 and T_2^* are expressed as follows:

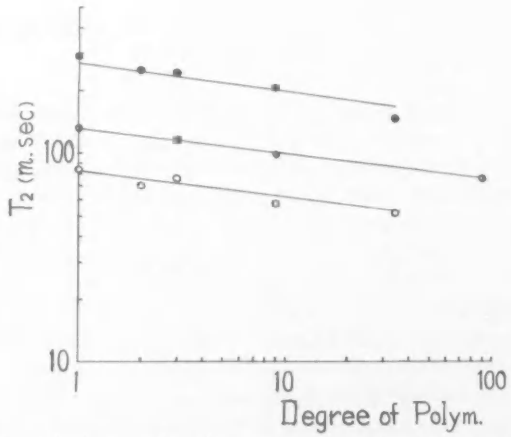

Fig. 1. Spin-spin interaction time vs. degree of polymerization of polyethylene glycol. (●) T_2^*, 295°K; (◑) T_2, 323°K; (○) T_2, 295°K.

$$1/T_2 \fallingdotseq \sigma_1^2 \tau_{c1} \fallingdotseq \sigma_1^2 \tau_{c1}$$
$$1/T_2^* \fallingdotseq (3/10)\,\sigma_1^2 \tau_{c1} + 1/T_2^{+} \fallingdotseq (3/10)\,\sigma_1^2 \tau_{c1} \qquad (3)$$

where $1/T_2^{+}$ is the contribution to line width from inhomogeneity of the applied magnetic field, and the subscripts 1 and 2 denote the contribution from methylenic and hydroxy protons, respectively. The factor 3/10 in eq. (3) is the ratio of adiabatic second moment to total one (3). The difference between T_2 and T_2^* at 295°K. is interpreted by this factor. The ratio 12.0/3.4 = 3.5, which is slightly different from theoretical value 10/3 = 3.33, may arise from the error introduced by the neglect of the second term in the right-hand side of eq. (3).

Provided that the correlation time as well as that of the liquid which is composed of molecules of radius ρ (4) is expressed,

$$\tau_c = 4\pi\eta\rho^3/3kT \qquad (4)$$

eq. (3) is written as

$$1/T_2 \fallingdotseq \sigma'^2_1 (4\pi a^3/3kT)\,\eta_{loc.} + \sigma''^2_1 (4\pi \langle\gamma^2\rangle^{3/2}/3kT)\,\eta \qquad (5)$$

where a is the radius of mobile unit in polymer chain, $\langle\gamma^2\rangle^{1/2}$ is the mean radius of gyration of a chain, η is the viscosity, and single and double primes denote intramolecular and intermolecular contributions, respectively. The symbol loc. of $\eta_{loc.}$ in eq. (5) denotes the viscosity

due to the micro-Brownian motion of a mobile unit which is distinguished from the usual one. This may be called local viscosity. Since the second term in the right-hand side of eq. (5) is much smaller than the first term, the approximation formula is given by

$$1/T_2 \fallingdotseq \sigma'^2_1 (4\pi a^3/3kT)\, \eta_{loc.} \tag{6}$$

Introducing the values of $\sigma'^2_1 = 3.5\ 10^{10}\text{sec.}^{-2}$ and a = 4.8 A. in eq. (6), the relations are

$$\begin{aligned} \eta_{loc.} &= 0.031\ n^{0.2}\ \text{(poise) at } 295°\text{K.} \\ \eta_{loc.} &= 0.024\ n^{0.2}\ \text{(poise) at } 323°\text{K.} \end{aligned} \tag{7}$$

It should be noted that these formulas are similar to those of molecular weight dependence of the melt viscosity and that our method for the measurement of local viscosity is more quantitative than that of Nishijima et al. (5).

Such a relation between spin-spin interaction time and degree of polymerization could be interpreted by another concept different from that of the local viscosity, namely, by the distribution of correlation time. Recently, Khazanovich (5) derived the relationship between T_2 and n by applying Rouse model to chain segment as follows:

$$1/T_2 = 1.08\ \sigma^2\ \tau_a \ln n - 0.126\ \sigma^2\ \tau_a \ln (\omega_0 \tau_a) \tag{8}$$

where τ_a is the least correlation time and ω_0 is the frequency used in the measurement. If $(1.08/0.126)\,[\ln n / \ln (\omega_0 \tau_a)]$ is much smaller than unity, eq. (8) is approximated into

$$1/T_2 = 0.126\ \sigma^2 \tau_a \ln (\omega_0 \tau_a)\ n^{-8.57 \ln (\omega_0 \tau_a)} \tag{9}$$

and the values

$$\begin{aligned} \tau_a &= 6.7 \times 10^{-11}\ \text{(sec.) at } 295°\text{K.} \\ \tau_a &= 4.3 \times 10^{-11}\ \text{(sec.) at } 323°\text{K.} \end{aligned} \tag{10}$$

are obtained by the comparison of eqs. (1) and (10).

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MECHANO-CHEMICAL POLYMERIZATION OF VINYL ACETATE

It has been known that a polymer molecule is ruptured by mechanical force and that the degree of polymerization decreases (1-7). Such a mechanical degradation has also been observed in a case of violently stirring a polymer dilute solution. Johnson and Price (4) have described the shear degradation of polystyrene and polyisobutylene in dilute solutions by high speed stirring. The present authors will report in respect to the rupture of polyvinyl acetate in dilute solution due to stirring and in respect to a vinyl polymerization to be initiated by a macroradical formed during the rupture of polymers.

With the use of a Homo-mixer (Tokushu Kika Kogyo Co. Ltd.) revolving at high speeds (30,000 rpm), PVAc-cyclohexanone or PVAc-VAc (25 g./l. solutions of 250 ml.) are agitated in nitrogen atmosphere or in air. The extent of degradation is evaluated with the intrinsic viscosity of the sheared PVAc. Effects of oxygen on the degradation of PVAc chain

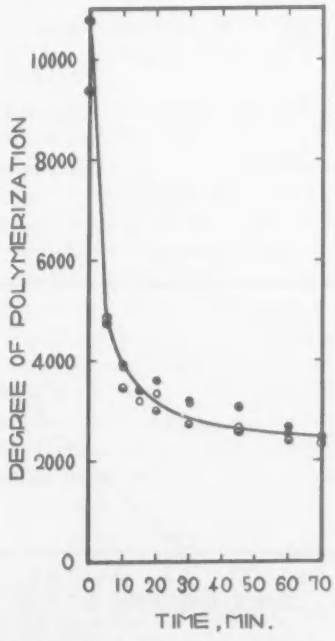

Fig. 1. Shear degradation of PVAc in cyclohexanone solution (25 g./l. concentration). (○) in air; (●), (◒) in nitrogen.

are shown in Figure 1. It may be concluded that the oxidative degradation of the chain is not so remarkable. Such a decrease in $[\eta]$ must result from a simple scission of C–C bonds by shearing force. Moreover, PVAc used in our investigation has been prepared by emulsion polymerization (the degree of polymerization was 10,800). However, DP broke down to 3,000 after shear (the limiting chain length decreases with the increase of the initial concentration of shearing polymer solution) (4,8).

If the mechanical degradation of polymers takes place within a vinyl monomer under nitrogen atmosphere, the monomer would be polymerized by fragments, such as macroradicals. Watson (2), Ceresa (10), and Berlin (11) have previously described these mechano-chemical reactions. In order to obtain quantitative information, the present authors have carried out a mechano-chemical polymerization on PVAc-VAc systems. For example, a VAc solution which contained various PVAc (250 ml.), did undergo a constant shear in a nitrogen atmosphere. The solution was elevated to a temperature of about 63 to 64°C., but was controlled by maintaining a constant temperature of 65°C. When PVAc was absent in the liquid, no polymerization occurred after one hour. Thermal polymerization of VAc was ignored during the agitation. This would never be accomplished if hydroquinone was added in the solution previously. Results in Table I designate this mechano-chemical polymerization.

Elemental expressions of the mechano-chemical polymerization are as follows:

$$P_0 \xrightarrow{kd} P_i^* + P_j^* \qquad \text{mechanical degradation} \qquad (1)$$

$$P_i^* + M \xrightarrow{k_i} P_{i+1}^* \qquad \text{initiation} \qquad (2)$$

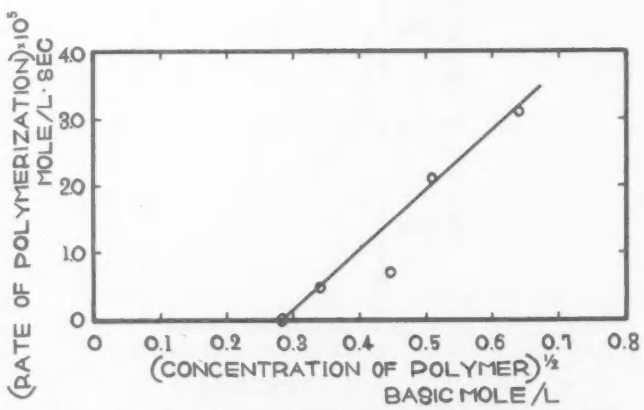

Fig. 2. Relationship of the rate of polymerization to the initial concentration of PVAc.

TABLE I

Mechano-chemical Polymerization of Vinyl Acetate

Concn. of polymer, (g./l.)	Concn. of polymer, (basic mole/l.)	(Concn. of polymer)$^{1/2}$, (basic mole/l.)	Rate of polymerization, (mole/l.sec.)
35.20	0.409	0.640	3.113×10^{-5}
22.5	0.262	0.512	2.087×10^{-5}
17.3	0.201	0.448	0.659×10^{-5}
9.77	0.114	0.338	0.456×10^{-5}
6.88	0.080	0.283	0.000

$$P_{i+1}^* + M \xrightarrow{k_p} P^* \qquad \text{propagation} \qquad (3)$$

$$P^* + M \xrightarrow{k_{trM}} P + M^* \qquad \text{transfer to monomer} \qquad (4)$$

$$P^* + P_0 \xrightarrow{k_{trP}} P + P_0^* \qquad \text{transfer to polymer} \qquad (5)$$

$$P_n^* + P_m^* \xrightarrow{k_t} P_{n+m} \text{ or } P_n + P_m \qquad \text{termination} \qquad (6)$$

$$v_p = (2k_d/k_t)^{1/2} k_p [M] [P_0]^{1/2} \qquad (7)$$

where v_p is the rate of polymerization, [M] is the concentration of monomer, $[P_0]$ is the initial concentration of PVAc (basic mole/l), and k_d, k_p, and k_t are the rate constant for each reactions. The expression suggests that the rate of polymerization was proportional to the square root of the initial concentration of PVAc. This relationship is confirmed in Figure 2. The straight line, however, does not go through the origin, but crosses the abscissa. This data assumes that, at 30,000 rpm, mechano-chemical reaction do not occur in a solution containing PVAc (P 10,800) (about 6.88 g./l.). When VAc solution which contained PVAc (6 g./l.) was prepared and was agitated with the Homo-mixer, VAc was not polymerized. The solution included many macromolecules, so that the mechano-chemical reaction, nevertheless, did not occur. It may be due to the fact that the limiting chain length of degradable PVAc increased as the concentration of the solution decreased.

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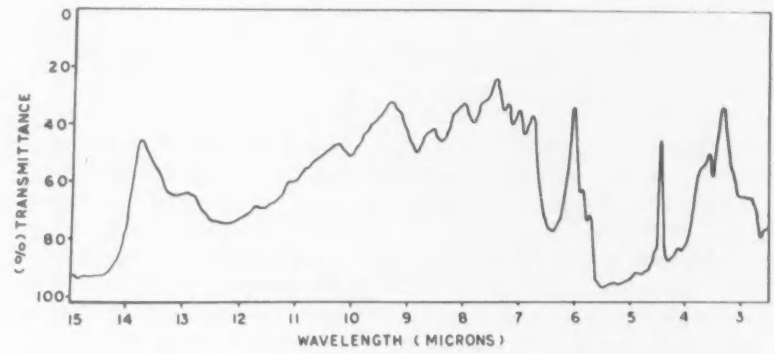
STUDIES ON CELLULOSE-POLYACRYLONITRILE GRAFTS

Polymerization of acrylonitrile in cellulosic materials has been studied extensively in recent years using different methods for initiating polymerization. Formation of a cellulose-polyacrylonitrile (PAN) graft is expected to occur. Evidence in support of this assumption is largely based on the altered solubility characteristics of cellulose and PAN. In a recent publication (1) we also showed considerable improvement in wet crease recovery of a PAN-cotton fabric system by a sequence of reactions in which the nitrile groups of PAN were changed to $-CO{\cdot}NH{\cdot}CH_2OH$, which was then reacted with the cellulose hydroxyls in the presence of magnesium chloride. This result, like the altered solubility characteristics, is not an unequivocal evidence of graft formation, since deposition of the homopolymer in the cellulose fiber could also be a possible explanation. More direct evidence supporting graft formation is presented here.

Acrylonitrile was polymerized in a cotton fabric as described earlier (1). The treated fabric was extracted with dimethyl formamide (DMF) and subsequently with 80% zinc chloride solution to remove the homopolymer. It was next treated overnight with cuprammonium hydroxide (CuAm) to remove ungrafted cellulose. The insoluble residue was filtered, washed with ammonia, neutralized, and washed. This was further given a mild hydrolysis with 1N HCl at 90°C. for 10 min. in order to break up the long cellulose chains into smaller fragments and facilitate extraction of the ungrafted fragments in a second CuAm treatment. The residue left insoluble after this second CuAm extraction was filtered, neutralized, washed, and dried.

This residue showed a strong reducing property when treated with Fehling's solution, indicating the presence of terminal aldehyde groups from parent cellulose backbones. It also showed a high percentage of nitrogen. Although it was very finely dispersed as a precipitate in the CuAm solution, it readily formed a tacky film on filtering out the excess CuAm solution. It was not soluble in DMF, 80% $ZnCl_2$, or CuAm. It was dark brown in color probably due to adsorption of copper. When extracted with 72% cold sulfuric acid overnight, it resisted degradation and was mostly insoluble. The filtrate, however, showed the presence of glucose when analyzed chromatographically, indicating a slow hydrolysis of the cellulose chains in the graft.

This final residue can only be the graft of cellulose with PAN. The initial extraction with DMF and $ZnCl_2$ reduced the PAN content of the fabric from 7.0 to 4.3%. 8.5 g. of the treated fabric at this stage (containing 0.36 g. of PAN) gave, after the sequence of treatments described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20
40
60
80
100
(%) TRANSMITTANCE
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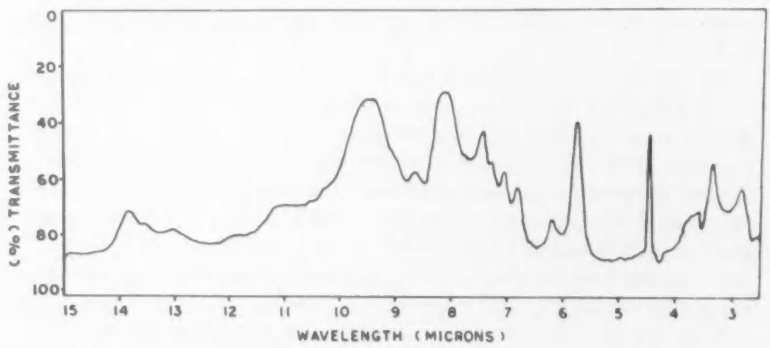
WAVELENGTH (MICRONS)

(a)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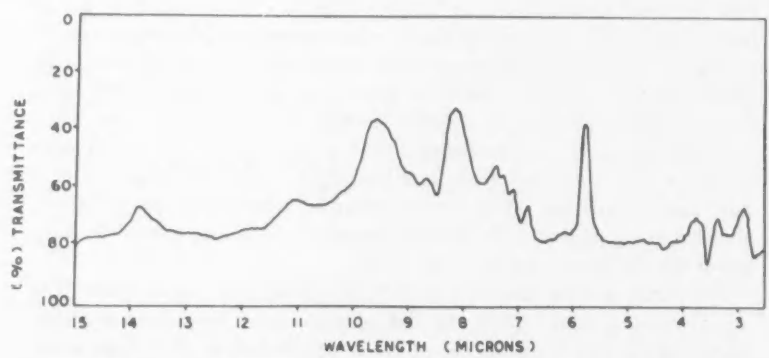
(b)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WAVELENGTH (MICRONS)

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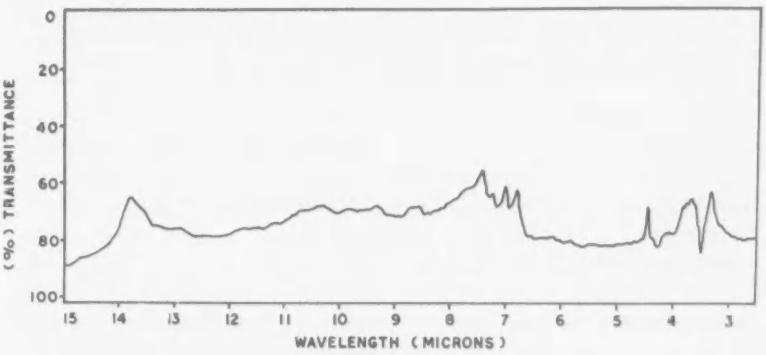

(d)

Fig. 1. Infrared spectra of cellulose acetate-PAN grafted sample: (a) graft corresponding to 3% cellulose acetate fraction in paraffin mull (composition 85% PAN-15% cellulose acetate); (b) physical mixture corresponding to 3% cellulose acetate fraction in paraffin mull (composition 85% PAN-15% cellulose acetate); (c) cellulose acetate 3% in paraffin mull; (d) PAN (3% in paraffin mull).

above, a final residue of 0.55 g. which contained 48.6% of its weight, i.e., 0.26 g. PAN. In other words, approximately 37% of the initial add-on of PAN and 72% of PAN add-on after thorough extraction of superficially deposited homopolymer was present as a graft with cellulose.

A sample of cellulose acetate-PAN graft was also prepared and isolated as described earlier (1). In Figure 1 (a-d) are shown the IR spectra of the isolated graft, a physical mixture of cellulose acetate and PAN, and the corresponding blanks. In Figure 1a the OH peak at 2.9 μ has considerably diminished in intensity, suggesting substitution of the available hydroxyls during graft formation. The ester peak at 5.8 μ has also been modified in the graft, with a shift from 5.8 to 6.0 μ with two additional shoulders at 5.8 and 5.9 μ. The nitrile peak at 4.4 μ has remained unchanged in the graft. The reduced intensity of the OH peak and the presence of the modified ester peak at 6.0 μ and of the nitrile peak at 4.4 μ indicate the presence of a cellulose acetate-PAN graft.

The authors wish to thank the Director and Council of Administration ATIRA for allowing them to publish this work.

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HIGH TEMPERATURE DEUTERATION OF CELLULOSE II

The authors have studied the improvement of rayon by high temperature steaming (1) and in a previous paper (2) some model experiments were reported. There, cellulose II film was heat-treated with D_2O or H_2O at 100-210°C. and measurement was made of the amount of resistant OD groups, ΔX_{OD}, or the increment of the non-accessible part to D_2O vapor of room temperature, X_{OH}, using the method of Mann and Marrinan (3), in order to trace the increase in crystallinity of the film caused by the D_2O or H_2O treatment. In the above measurements an assumption was made that the deuteration or rehydrogenation occurred only in the amorphous region of cellulose and this assumption seemed right because ΔX_{OD} was obtained in an amount nearly equal to the increment of X_{OH}. However, a recent study shows that this assumption is not

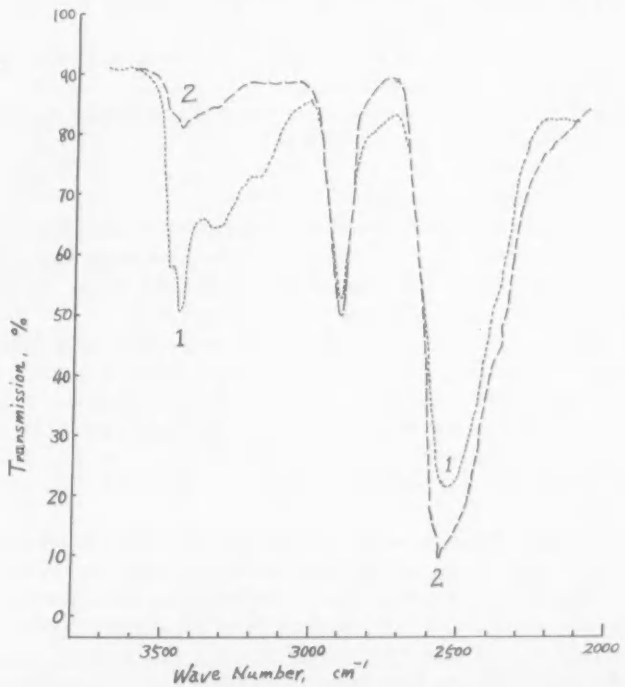

Fig. 1. Decrease in amount of the nonaccessible OH groups to D_2O at high temperature: (1) deuteration (vapor) at room temperature for 6 hr.; (2) deuteration (liquid) at 210°C. for 7 min. (see Table I).

TABLE I

Change in the Resistant OD Groups (ΔX_{OD}) and the Nonaccessible Part (X_{OH}) to D_2O Vapor by Heat Treatment with Heavy Water

Condition of treatment		ΔX_{OD}, [a]	X_{OH}, [b]
°C.	Min.	%	%
170	5 [c]	12.3	10.9
170	10 [c]	13.3	7.7
170	20 [c]	13.3	8.6
170	30 [c]	12.2	7.2
210	7 [d]	17.8	3.7
220	5 [d]	18.1	4.2
Untreated		–	20.2

[a] Heat treated with liquid D_2O and rehydrogenated with liquid H_2O for 3 hr. at 25°C.

[b] The heat treated with liquid D_2O and rehydrogenated film was again deuterated with D_2O vapor for 6 hr. at 25°C.

[c] Approximately 2.5 min. is required to warm the content of the autoclave to the temperature in the first line.

[d] Approximately 5 min. is required to warm the content of the autoclave to the temperature in the first line.

correct at such high temperature.

In Figure 1 the curves are the IR spectrographs of a cellulose II film after 6 hr. deuteration at room temperature; 1 being a virgin film, while 2 had been heat-treated with liquid D_2O at 210°C. for 3 min. A remarkable decrease in X_{OH} can be seen on 2 compared with 1.

Some data indicating the effect of treating temperature with liquid D_2O upon X_{OH} and ΔX_{OD} of cellulose II film is listed in Table I, where it is to be noted that an increase in ΔX_{OD} follows a decrease in X_{OH} and the sum of ΔX_{OD} and X_{OH} is nearly constant and slightly larger than X_{OH} of the original film. The levelled-off amount of X_{OH} (cf. the experiment at 170°C.) is probably a function of the temperature of treatment.

The resistant OD groups show considerable resistance to rehydrogenation at room temperature, losing, however, much of their resistivity at higher temperatures, as can be seen in Tables II and III. Deuteration and rehydrogenation seem to reach the crystalline region of cellulose II rather easily at such higher temperature.

In the above study the experiments were carried out in a manner similar to that described in the previous paper (2). Further study on this subject is being conducted.

TABLE II

Rehydrogenation of Resistant OD Groups at Room Temperature

Condition of heat treatment with D_2O		Soaking time in H_2O,	ΔX_{OD},
°C.	min.	hr.	%
100	30	0	5.8
		3	5.0
		25	5.5
130	5 [a]	0	9.1
		3	6.2
130	10 [a]	0	10.6
		3	7.4
130	30 [a]	0	13.5
		3	10.9
150	30 [a]	0	11.3
		3	9.4
170	5 [a]	0	13.7
		3	9.9
		3 + 3	9.1
170	10 [a]	0	15.7
		3	13.3
		3 + 3	12.1
170	30 [a]	0	15.3
		3	12.2
		25	12.1
220	5 [b]	0	18.9
		25	18.1

[a] Approximately 2.5 min. is required to warm content of the autoclave to the temperature in the first line.

[b] Approximately 5 min. is required to warm the content of the autoclave to the temperature in the first line.

TABLE III

Rehydrogenation of Resistant OD Group at High Temperature

Condition of heat treatment with D_2O		Soaking time in H_2O at room temp.,	Heat treatment with liquid H_2O		ΔX_{OD},
°C.	min. [a]	hr.	°C.	min. [a]	%
130	5	3	–	–	6.2
		3	130	5	2.3
150	30	3	–	–	9.4
		3	170	5	1.1
170	5	25	–	–	11.3
		25	150	5	5.1
170	20	25	–	–	12.5
		25	170	20	3.5
170	30	25	–	–	12.1
		25	170	10	2.2

[a] Approximately 2.5 min. is required to warm content of the autoclave to the temperature in the first line.

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POLYMER LETTERS VOL. 1, PP. 517-519 (1963)

ORGANOTIN CHEMISTRY. V.* POLYDIORGANOTIN OXIDES— THERMAL BEHAVIOR AND PHYSICAL PROPERTIES

Reichle (1) has previously examined the thermal and chemical behavior of several dialkyltin oxides and diphenyltin oxide, and has characterized these materials as high melting, fairly crystalline, and essentially insoluble in most of the common solvents (with the exception of dioctyltin oxide which is toluene soluble). We wished to determine whether his observations extended to a more complete series of dialkyl- and diaryltin oxides.

Experimental

Most of the polydialkyl- and diaryltin oxides were available as samples from our stock. Tin analyses on these materials showed them to be of acceptable purity. These materials were all prepared by basic hydrolysis of the appropriate diorganotin dihalide followed by exhaustive washings with water, isopropanol, and acetone.

Ditertiarybutyltin dihydroxide was prepared essentially by the method of Krause and Weinberg (2) from ditertiarybutyltin dichloride. In our hands, the pure dihydroxide could not be prepared, but rather a low polymer (average DP 1.4) was formed.

Both thermogravimetric analysis and differential thermal analysis were carried out in self-constructed units. Heating rate for the TGA furnace was 14°C./min., and for the DTA furnace was 8.9°C./min. Calcined Al_2O_3 (Norton, Grade 22OX) was used as the reference material for DTA analyses.

All analyses were carried out in a static air atmosphere.

Visual decomposition points were determined using an open capillary tube in a Mel-Temp. Apparatus (Laboratory Devices, Cambridge, Mass.) which was uncalibrated. Heating rate was 6°C./min. and decomposition was evidenced either by darkening of the sample, or partial melting followed by gas evolution. Visual decomposition temperatures proved to be erratic, giving either low or high results compared to the other methods.

Molecular weight determinations were carried out in a thermistor osmometer (Mechrolab Osmometer Mod. 301).

No attempt was made to identify the degradation products. Reichle (1) has found the degradation under nitrogen of dioctyltin oxide to yield 1-octene as the major organic decomposition product.

*Paper IV, Gerald A. Baum and Wm. J. Considine, to be published in J. Org. Chem.

Results and Discussion

Table I shows that the most thermally stable groups are methyl and phenyl. Stability then decreases through propyl and alternates through butyl, amyl, and octyl. In the butyltin oxide series, the stability order is primary > secondary > tertiary. In the propyltin oxide series, isopropyl is more stable than n-propyl. The reason for this difference is not clear.

Attaching a second alkyl group to a carbon not directly connected to a tin atom appears to increase stability; isobutyl being more stable than n-butyl, and 2-ethylhexyl more stable than n-octyl.

Unsaturates are seen to decompose at lower temperatures than their saturated analogs. Divinyltin oxide decomposes at 210°C., while diethyltin oxide decomposes at 225°C.. Diallyltin oxide decomposes at 180°C., while di-n-propyltin oxide decomposes at 210°C. Dibenzyltin oxide is much less stable than diphenyltin oxide.

In order to determine the effect of the negative radical attached to tin, the TGA of dibutyltin sulfide was also determined and found to be about 260°C. or 30°C. higher than the corresponding dibutyltin oxide. This is interesting because the sulfide is a liquid, a cyclic trimer (3), while the

TABLE I

Thermal Decomposition Data for Dialkyl and Diaryltin Oxides

Compound	Visual m.p., °C.	Visual decomp., °C.	TGA initial decomp., °C.	DTA initial decomp., °C.
Me_2SnO	–	375-395	360	310
Et_2SnO	–	350	225	230
n-Pr_2SnO	–	290-310	210	210
i-Pr_2SnO	265	265	250	270
n-Bu_2SnO	340	310	230	225
i-Bu_2SnO	270	285	245	230
s-Bu_2SnO	185	250	200	220
t-$Bu_2Sn(OH)_2$	250	250	190	180
n-$(Amyl)_2SnO$	325	250	190	190
n-Oct_2SnO	285	295	250	270
$(2\text{-Et-hexyl})_2SnO$	Semi-solid	225	290	160
$(Vinyl)_2SnO$	–	205	210	215
$(Allyl)_2SnO$	–	150	180	110
Φ_2SnO	350	350	340	390
$(Benzyl)_2SnO$	80	110	160	120

oxide is a solid, relatively high molecular weight polymer. This would indicate that the tin–sulfur bond is more thermally stable than the tin–oxygen bond.

The thermal and physical behavior of certain of the branched dialkyltin oxides is at variance with the straight chain compounds. Visual observation of decomposition temperatures indicated that several of the branched chain compounds had relatively low melting points (as shown in Table I) which were sharp and reproducible, although DTA data indicated slight decomposition at or near the melting point.

Di-isobutyltin oxide showed no change in crystal structure as determined by x-ray analysis upon melting and cooling to room temperature. Di-sec-butyltin oxide, after melting and cooling showed a decrease in crystallinity, which might be indicative of further polymerization during the melting process.

Several of the branched chain derivatives also exhibited relatively good solubility in organic solvents. Di-sec-butyltin oxide was found to be easily soluble in THF and chloroform. The compound could also be prepared in ether, but if the solution was allowed to evaporate to dryness, the residue was no longer appreciably soluble in ether, probably due to further polymerization.

Di-tert-butyltin dihydroxide was soluble in THF and chloroform. It was slightly soluble in hot ether and acetone. The compound was also fairly soluble (about 10%) in water when freshly prepared, but on standing solubility decreased to 1–2%.

Both di-isopropyl- and -isobutyltin oxide were insoluble in all common solvents tried.

Molecular weight determinations as carried out on the secondary and tertiarybutyltin derivatives (in chloroform) indicated a molecular weight of 610 (average DP of 2.3) for the secondary derivative, and a molecular weight of 365 (average DP of 1.4) for the tertiary derivative. This would indicate that branched-chain diorganotin oxides are lower molecular weight polymers of increased solubility compared to their straight-chain analogs.

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CORRELATIONS OF HAMMETT SIGMA VALUES WITH LOG REACTIVITY RATIOS IN VINYL POLYMERIZATIONS

Apparent deviations from the linear correlation (1,2) of Hammett sigma values with the log of the relative reactivity for electron donor nuclear substituted styrenes has been noted (3) in a study of the reactivity ratio and e values of p-methylstyrene. It was suggested that the values for p-dimethylamino and p-methoxystyrene be re-examined to remove this uncertainty. We have now done so and wish to record the data. The values of the monomer reactivity ratios for the styrene/p-methoxystyrene pair are $r_1 = 1.05$ and $r_2 = 0.79$ and for the styrene/p-dimethylaminostyrene pair are $r_1 = 0.89$ and $r_2 = 0.62$ as determined using the previously described (3) radioactivity assay for copolymer analysis. These values are in only fair agreement with values reported previously (1,2): $r_1 = 1.16$, $r_2 = 0.82$ (p-methoxystyrene) and $r_1 = 1.01$, $r_2 = 0.84$ (p-dimethylaminostyrene). The data presently reported are based on more complete analytical data and are perhaps more reliable. With these values and those previously reported for p-methylstyrene, e values of -1.55, -1.26, and -1.21 are obtained for p-dimethylamino, p-methoxy, and p-methylstyrene, respectively. This places the e values in the sequence which accords with their commonly accepted decreasing electron donor character. Using sigma values from one reaction type (4) (ionization of substituted benzoic acids) a plot of log reactivity ratio against this sigma value gives a plot with two linear regions of different slope. Below 0.0 sigma (electron donor substituents) the slope is zero. It appears, therefore, that electrostatic effects operate differently in determining the reactivity of styrene radicals with electron donor substituents than they do in determining the reactivity of styrene radicals with electron attracting substituents.

The authors are indebted to the U. S. Department of Health, Education, and Welfare for support of this study through a National Defense Fellowship held by one of us (B. D.) and to the U. S. Atomic Energy Commission for partial support through equipment made available under Contract AT-(40-1)-229.

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Sigma values are −0.83, −0.268, and −0.17 for p-dimethylamino, p-methoxy, and p-methyl, respectively.

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COPOLYMERIZATION PARAMETERS OF SYSTEM α-CHLOROACRYLONITRILE – STYRENE

In the course of an investigation on α-substituted acrylonitriles, we have studied the behavior of the copolymerization of α-chloroacrylonitrile with styrene.

The reactivity ratios r_1 and r_2 and the parameters Q_1 and e_1 of α-chloroacrylonitrile were determined. We have prepared this monomer from acrylonitrile by addition of chlorine and successive dehydrochlorination of the dichloroderivate obtained.

The dehydrochlorination was carried out simply by heating and stripping the dichloro compound rather than by reaction with basic compound such as AcONa (1), Na_2HPO_4 (2), and KCN (3). The product, purity grade 99.9%, had b.p. = 88–89°C., $n_D^{20} = 1.4297$, $n_D^{32} = 1.4205$, and $d^{20/4} = 1.06$.

The monomers were freshly distilled prior to use in a nitrogen current. The mixture of monomers with 0.1 wt.–% benzoyl peroxide was introduced into a Pyrex tube which was sealed under a purified nitrogen atmosphere. Copolymerization was performed in a thermostatic bath at 80 ± 0.1°C. and stopped after 1–3% conversion.

The copolymer was precipitated in methanol and purified by repeated dissolution in methyl- ethyl- ketone and precipitation in methanol.

After drying the copolymer composition was determined by nitrogen

TABLE I

Experimental Copolymerization Data of α-Chloroacrylonitrile–Styrene System

f_1	Conv., %	% N in copolymer	F_1
0.024	1.22	3.15	0.226
0.059	1.41	4.85	0.341
0.117	1.40	5.51	0.384
0.173	3.08	5.88	0.409
0.229	2.41	6.23	0.431
0.337	2.16	6.60	0.455
0.442	2.34	7.06	0.484
0.545	3.22	7.35	0.503
0.731	1.03	8.31	0.563
0.915	0.93	9.29	0.623

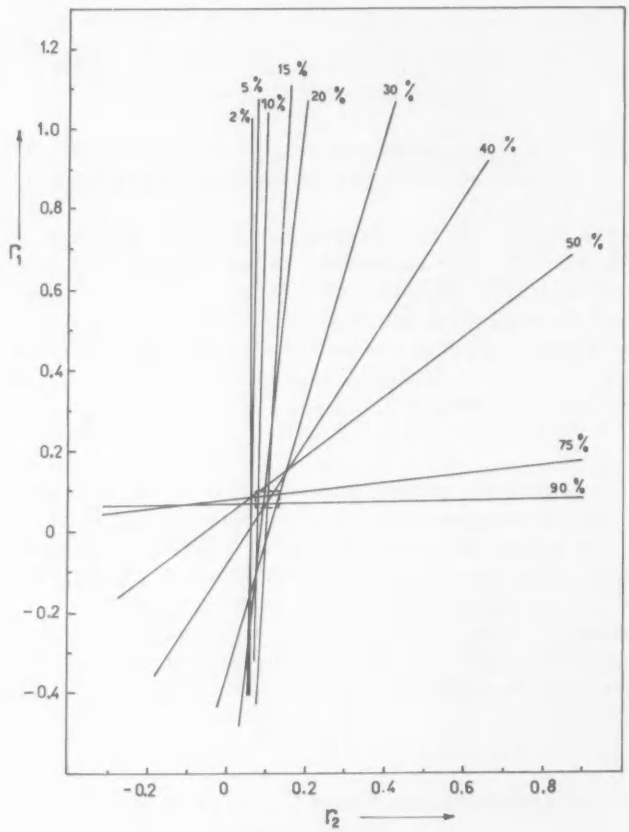

Fig. 1. r_1/r_2 Diagram.

analysis using the improved Kjeldahl method: to 0.3 g. of copolymer was added 20 cc. H_2SO_4 (98%) and 0.020 g. of selenium powder. This solution was heated to the boiling point until it became clear (approximatively 8–9 hr.). Working in this way, the error in the nitrogen determination is less than 0.1%. Experimental data are given in Table I. Molar fractions of the α-chloroacrylonitrile in the monomers mixture and in the copolymer are expressed as f_1 and F_1, respectively.

Reactivity ratios were calculated by the method of Mayo and Lewis (4) and the following values were found: $r_1 = 0.08 \pm 0.02$; $r_2 = 0.1 \pm 0.03$ (Fig. 1). Calculation of the parameters e_1 and Q_1 for α-chloroacrylonitrile based on the more recent data for styrene (5), $e_2 = -0.8$ and $Q_2 = 1.0$, gave: $e_1 = +1.396$ and $Q_1 = 8.38$.

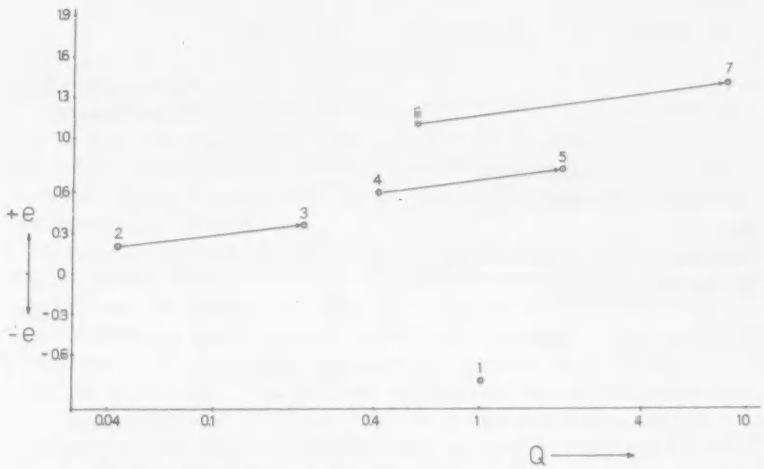

Fig. 2. Q-e map: effects of a chlorine atom on the double bond. (1) Styrene, (2) vinyl chloride, (3) vinylidene chloride, (4) methyl acrylate, (5) methyl-α-chloroacrylate, (6) acrylonitrile, and (7) α-chloroacrylonitrile.

Introduction of a chlorine atom in the α-position in the acrylonitrile leads to a more positive e value and a higher Q value. This displacement generally occurs when a hydrogen atom has been replaced by a chlorine atom in a vinyl monomer. The comparison between e and Q data (6) for vinyl chloride and vinylidene chloride, methyl acrylate and methyl-α-chloroacrylate, and acrylonitrile and α-chloroacrylonitrile shows the influence of a chlorine atom, electron-withdrawing substituent, which moderately activates the double bond (Fig. 2).

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The Twelfth Canadian High Polymer Forum will be held at the Cardy Alpine Inn, Ste. Marguerite, Quebec, on May 27-29, 1964. The Forum is sponsored by the National Research Council of Canada in co-operation with the Chemical Institute of Canada, and is devoted to all aspects of Macromolecular Science.

The Forum Lecturer will be Professor Charles Sadron, director of the Centre de Recherches sur les Macromolécules, Strasbourg, France. The Chairman of the Forum is Dr. David A. I. Goring, Pulp and Paper Research Institute, McGill University, Montreal, Quebec.

Authors wishing to submit papers for presentation at the Forum are asked to write to the Program Chairman, Dr. Leo Breitman, Research and Development Division, Polymer Corporation Limited, Sarnia, Ontario. Titles and abstracts of 200-300 words are required by February 15, 1964.

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